

High Energy X-ray Diffuse Scattering

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Acknowledgements

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Argonne National Laboratory*



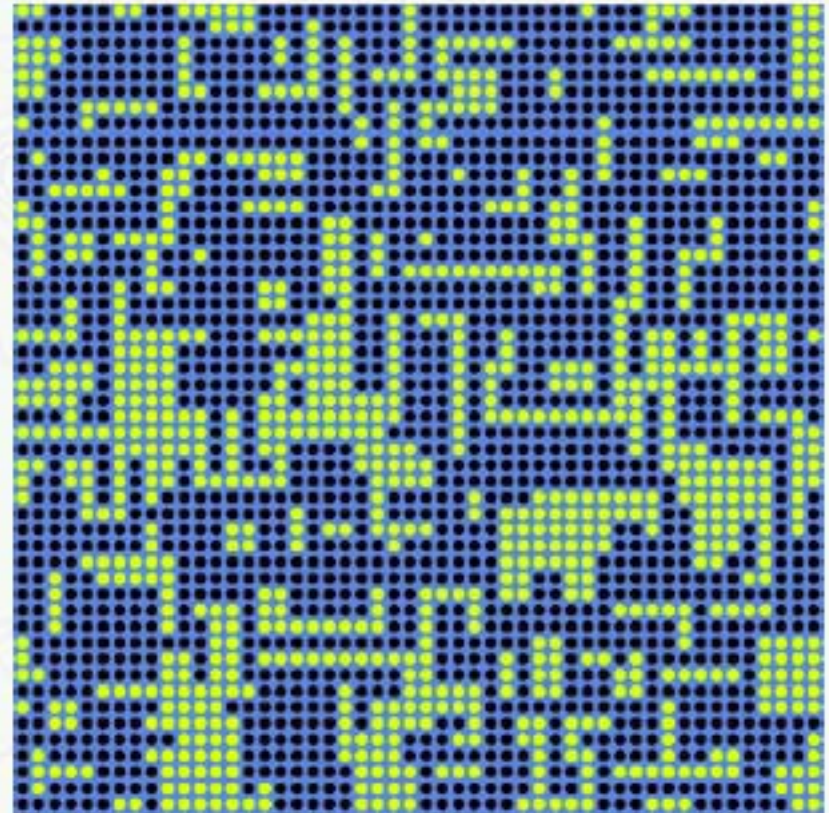
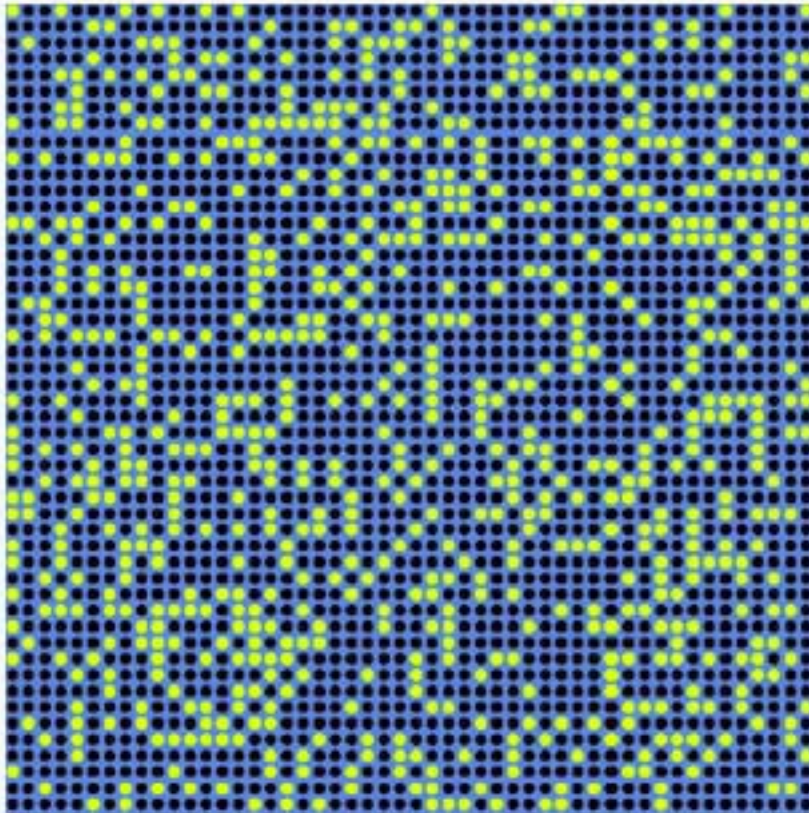
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Outline

- **Introduction to Single Crystal Diffuse Scattering**
 - Examples of Single Crystal Diffuse Scattering
 - *Metallic Alloys, Molecular Solids, Vacancy Complexes*
- **Diffuse Scattering in CMR Transition Metal Oxides**
 - Orbital Polarization (Huang Scattering)
 - Orbital Correlations (Longitudinal Jahn-Teller Modulations)
 - Correlated Polaronic Fluid
- **Potential and Demands of High-Energy X-ray Diffuse Scattering**
 - Efficient Measurement of Reciprocal Space Volumes
 - Data Analysis Techniques
 - Corrections for Thermal Diffuse Scattering
- **Conclusions**

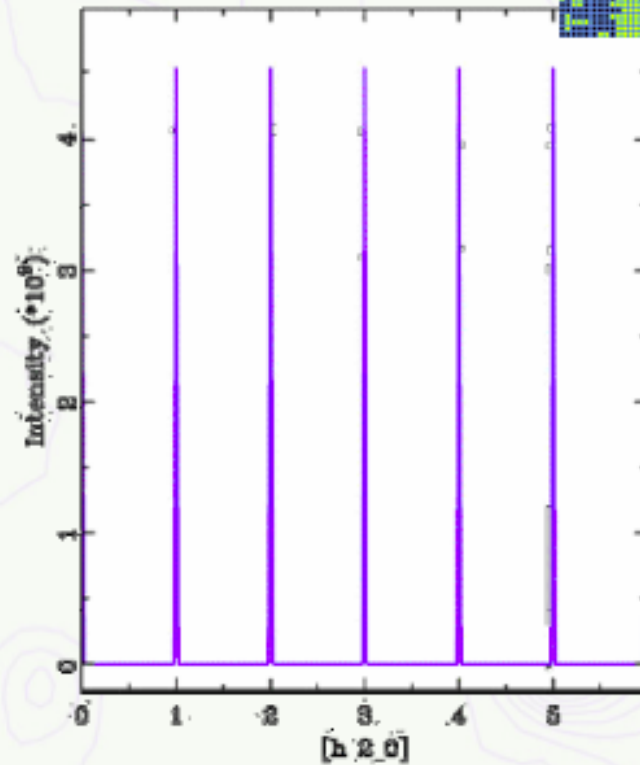
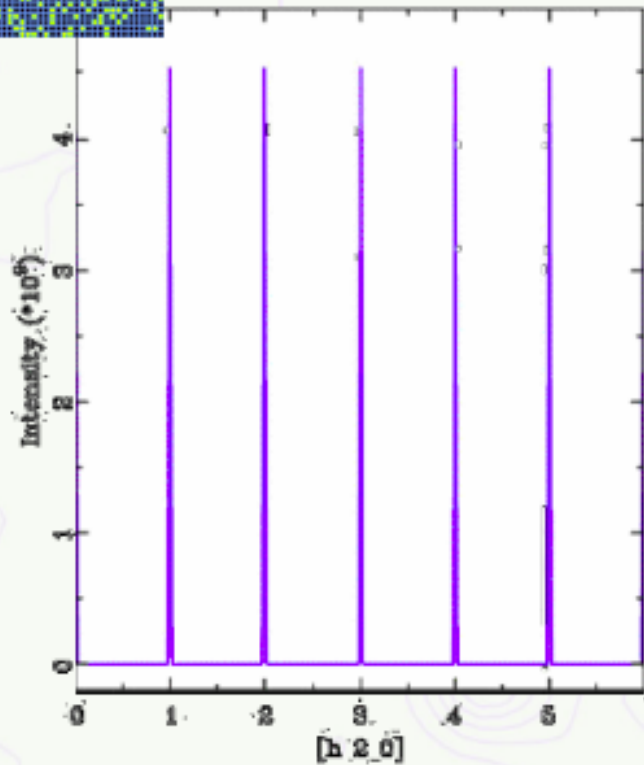
Importance of Diffuse Scattering



Cross section of 50x50x50 u.c. model crystal consisting of 70% black atoms and 30% vacancies !
Properties might depend on vacancy ordering !!

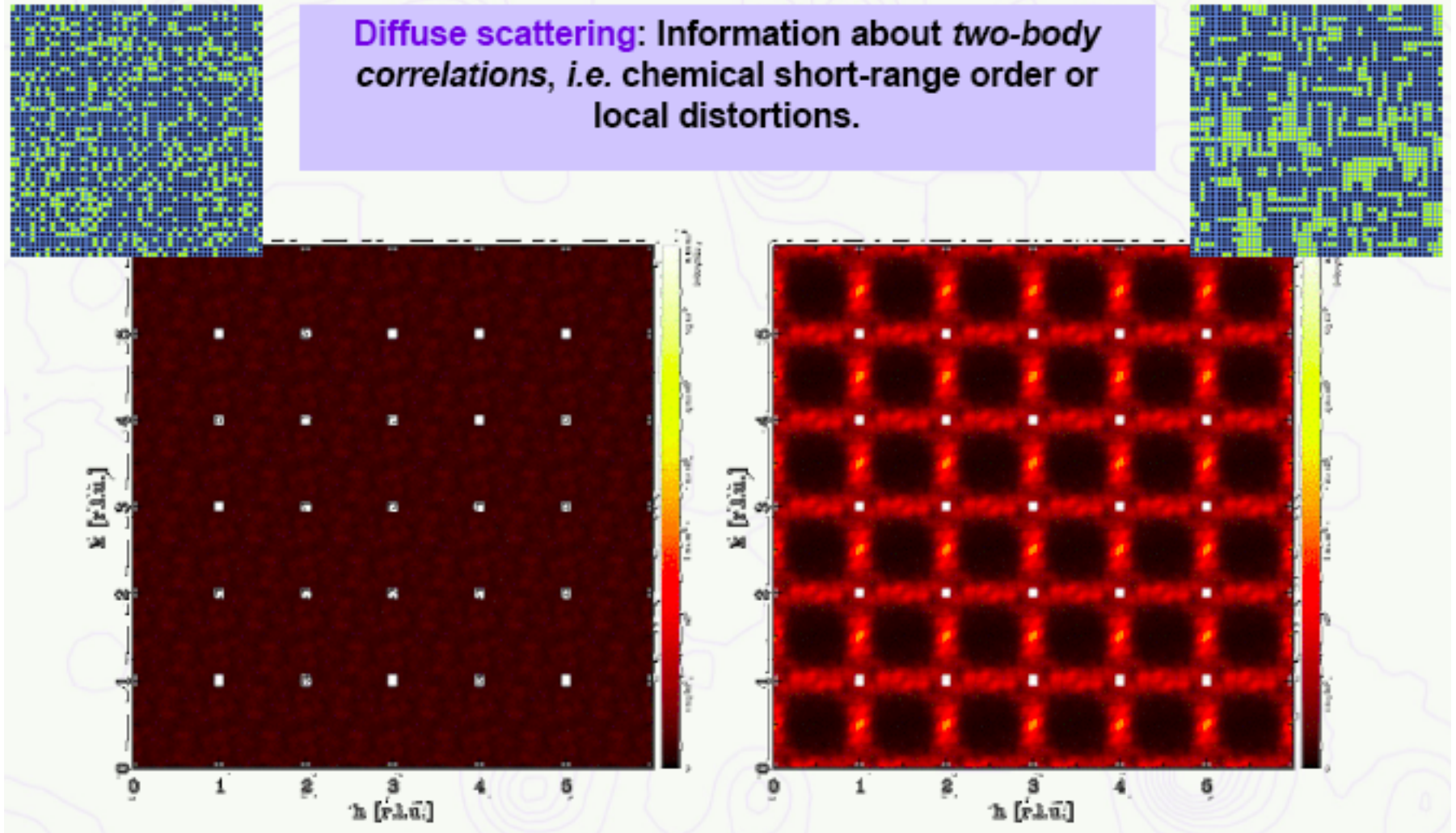
Bragg Scattering

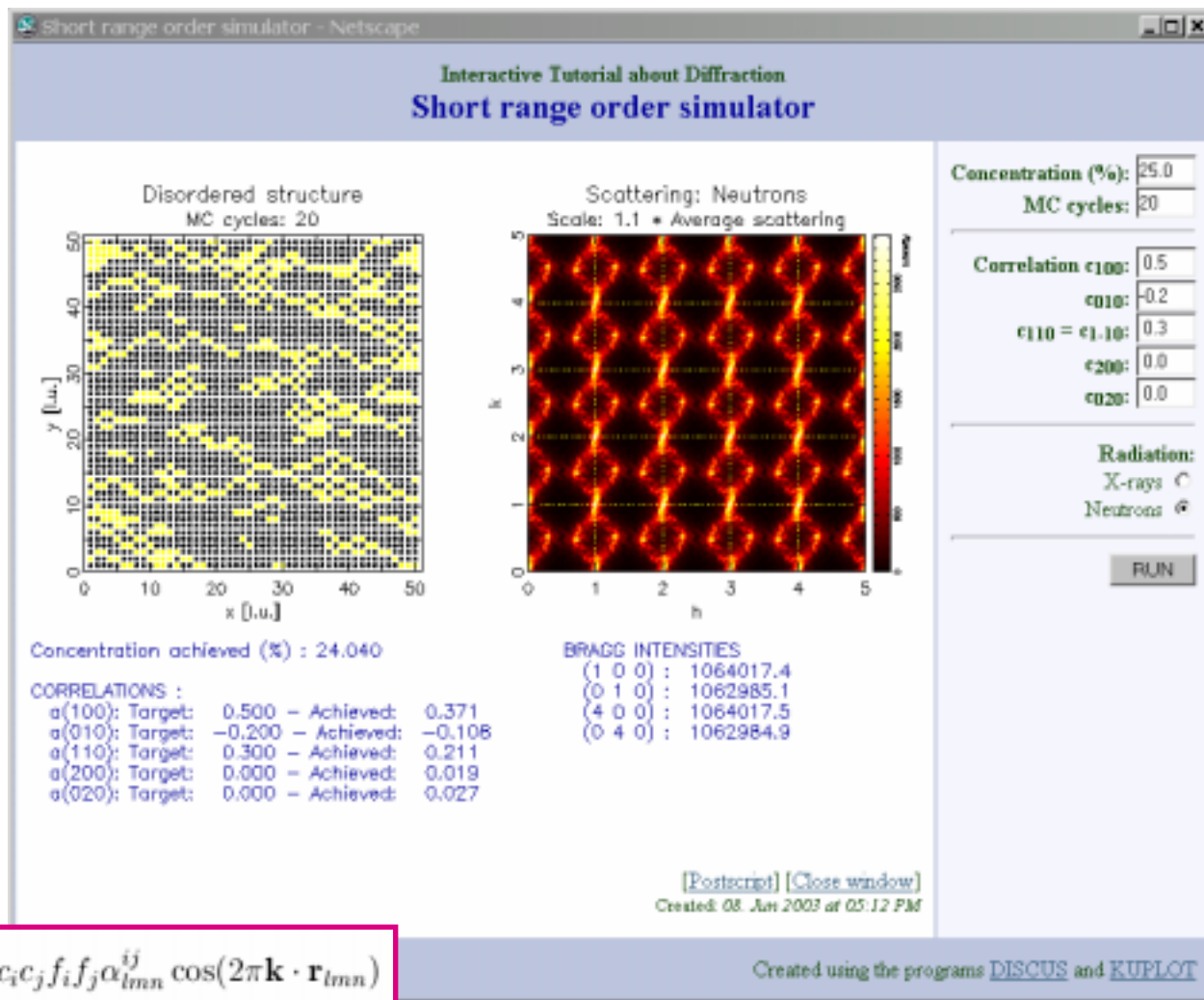
Bragg scattering: Information about the average structure, e.g. average positions, displacement parameters and occupancies.



Diffuse Scattering

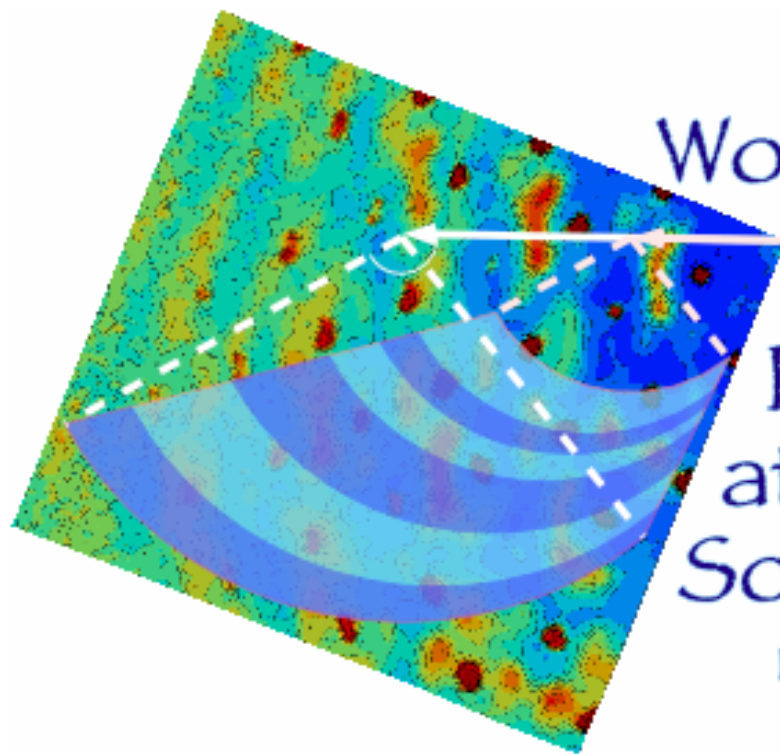
Diffuse scattering: Information about *two-body correlations*, i.e. chemical short-range order or local distortions.





$$I_{\text{SRO}} = - \sum_{ij} \sum_{lmn} c_i c_j f_i f_j \alpha_{lmn}^{ij} \cos(2\pi \mathbf{k} \cdot \mathbf{r}_{lmn})$$

Diffuse Scattering Workshop



Workshop on
“Single-Crystal
Diffuse Scattering
at Pulsed Neutron
Sources” June 16-17, 2003

Intense Pulsed Neutron Source
Argonne National Laboratory

[<http://www.neutron.anl.gov/diffuse/>](http://www.neutron.anl.gov/diffuse/)



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of Energy

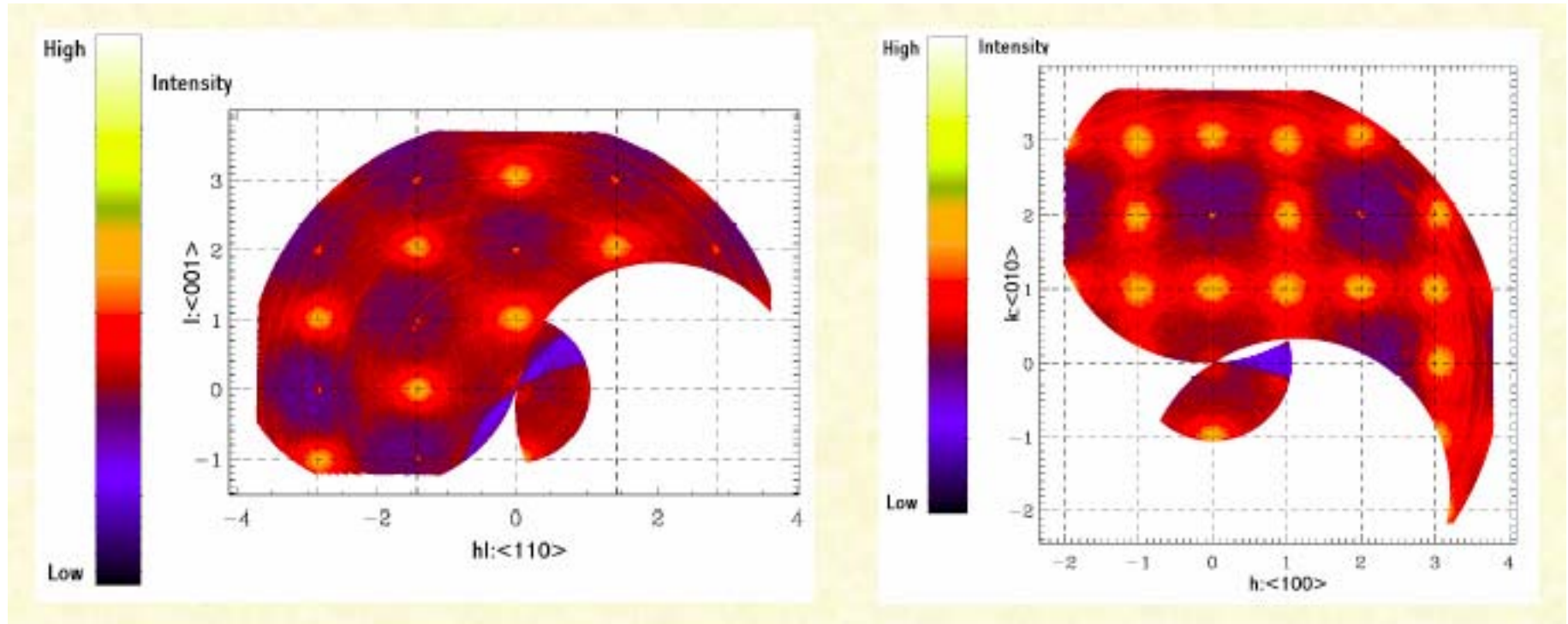


Scientific Scope of Diffuse Scattering

- List of subjects identified at the *Workshop on Single Crystal Diffuse Scattering at Pulsed Neutron Sources*
 - Stripes in cuprate superconductors
 - Orbital correlations in transition metal oxides (including CMR)
 - Nanodomains in relaxor ferroelectrics
 - Defect correlations in fast-ion conductors
 - Geometrically frustrated systems
 - Critical fluctuations at quantum phase transitions
 - Orientational disorder in molecular crystals
 - Rigid unit modes in framework structures
 - Quasicrystals
 - Atomic and magnetic defects in metallic alloys
 - Molecular magnets
 - Defect correlations in doped semiconductors
 - Microporous and mesoporous compounds
 - Host-guest systems
 - Hydrogen-bearing materials
 - Soft matter - protein configurational disorder using polarization analysis of spin-incoherence
 - Low-dimensional systems
 - Intercalates
 - Structural phase transitions in geological materials



Diffuse Scattering from Metallic Alloys

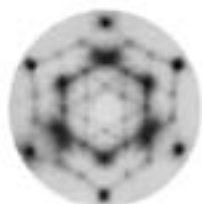


***Short-range Order in Null Matrix $^{62}\text{Ni}_{0.52}\text{Pt}_{0.52}$
measured on the DCS TOF spectrometer***

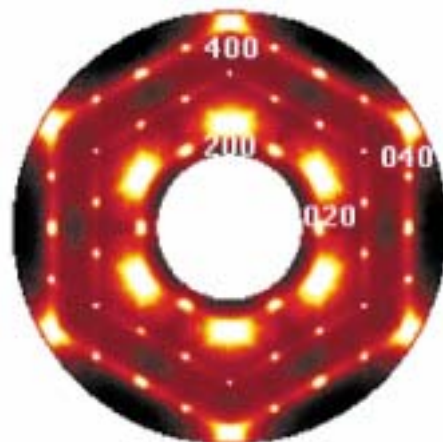
J. A. Rodriguez, S. C. Moss, J. L. Robertson, J.R.D. Copley, D. A. Neumann, J. Major, H. Reichert and H. Dosch

Diffuse Scattering from Molecular Solids

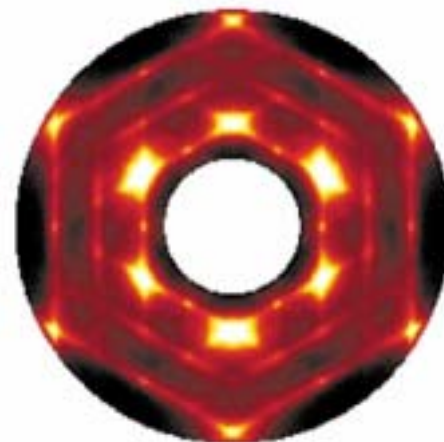
Benzil - $\text{C}_{14}\text{H}_{10}\text{O}_2$



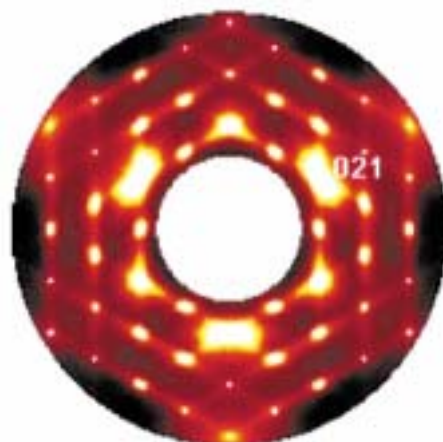
1941



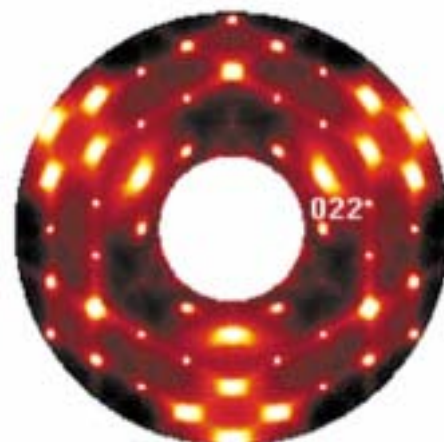
(a) Section $h \& 0.0$



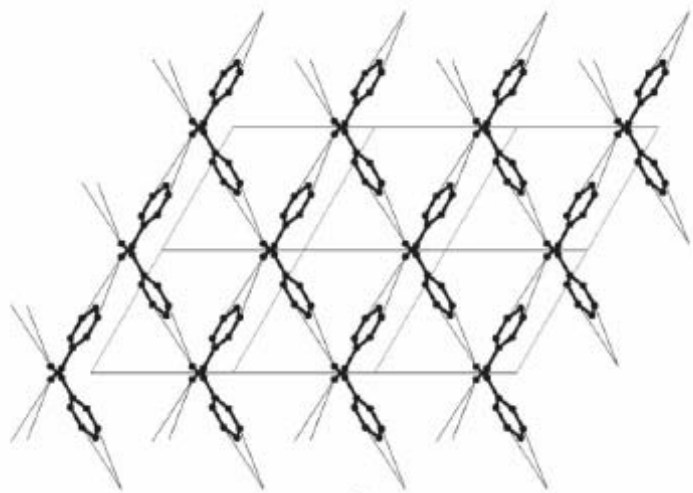
(b) Section $h \& 0.5$



(c) Section $h \& 1.0$



(d) Section $h \& 2.0$

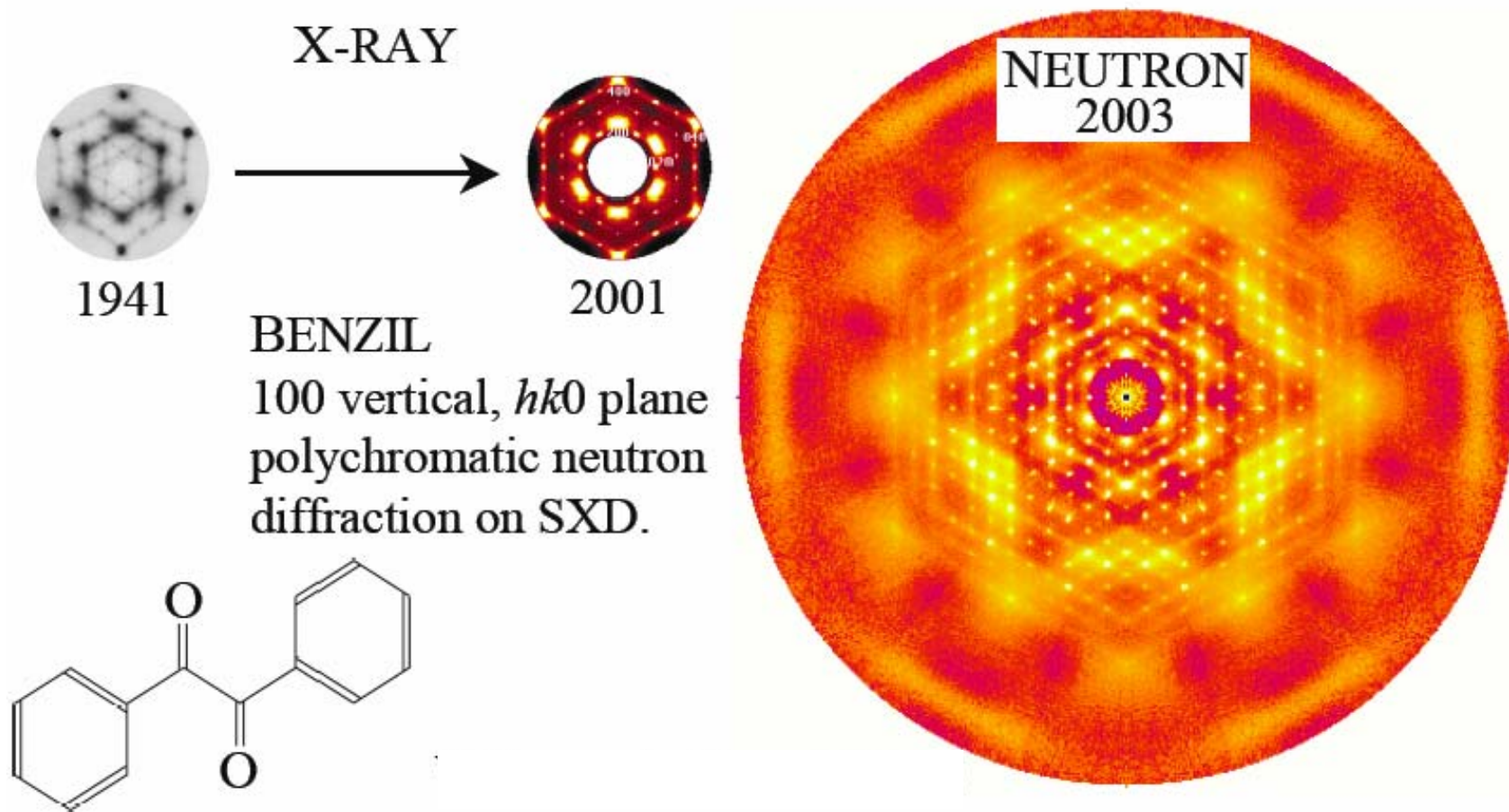


T. R. Welberry *et al* Acta. Cryst. A67, 101 (2001)

$2\theta = 26^\circ\text{-}77^\circ$ $\text{CoK}\alpha$

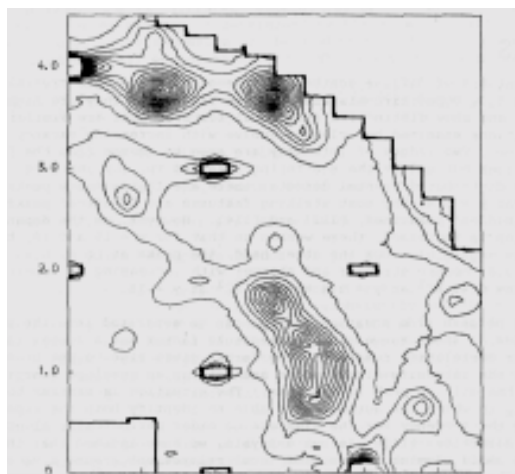


Diffuse Scattering from Molecular Solids



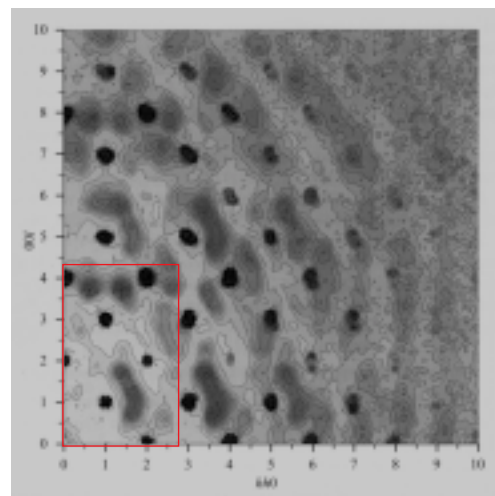
T. R. Welberry *et al* J. Appl. Cryst. **36**, 1400 (2003)

Diffuse Scattering from Vacancy Complexes

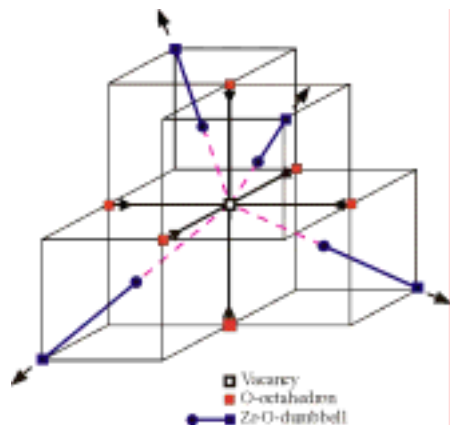


Triple-Axis data c 1983

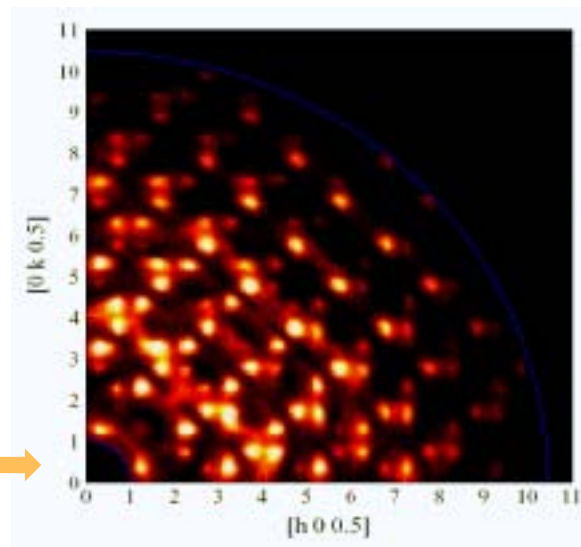
ISIS SXD data c 1998



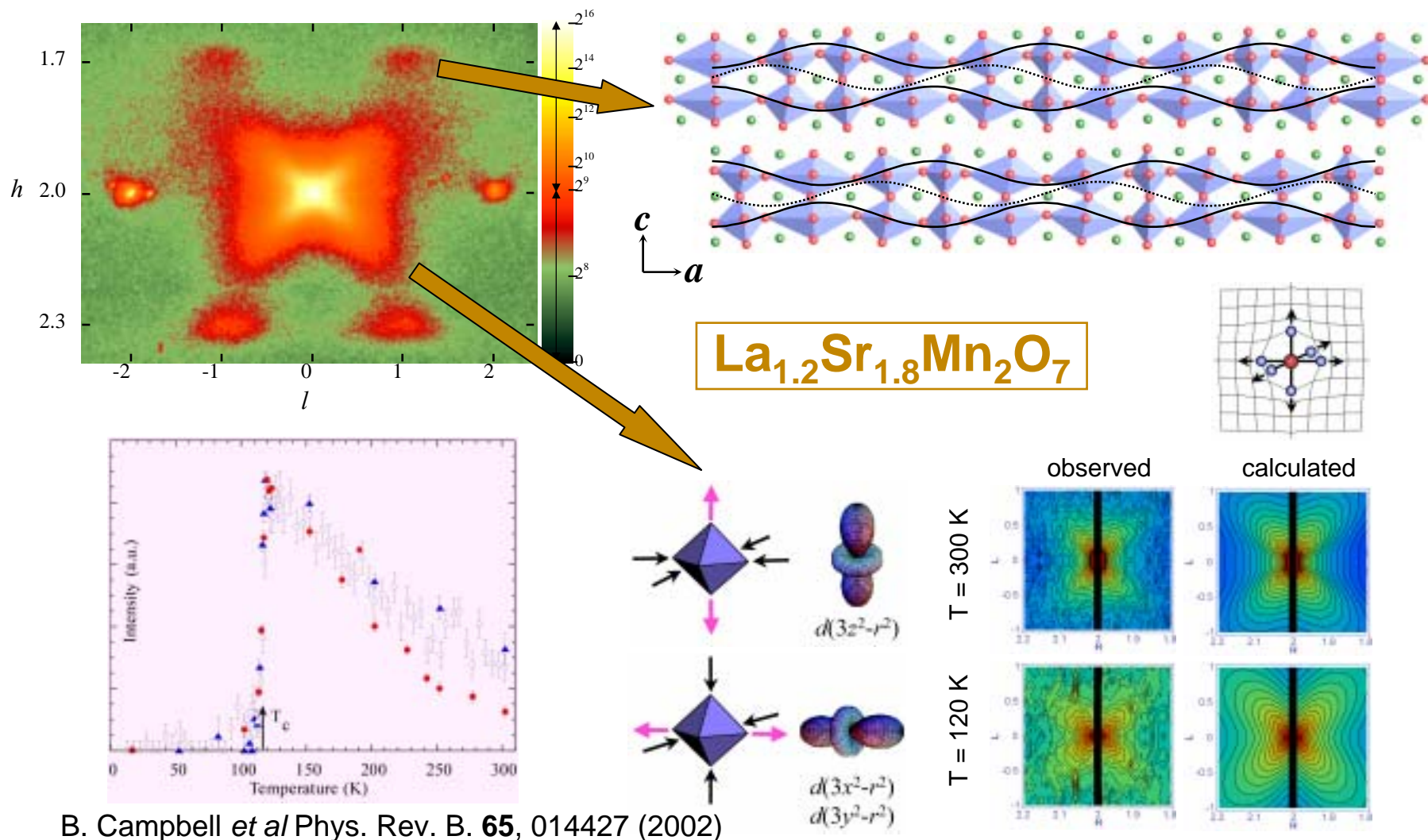
Cubic-Stabilized Zirconia



MoK α data



Diffuse Scattering from Transition Metal Oxides



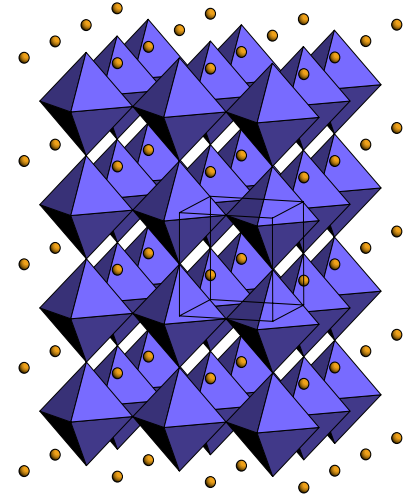
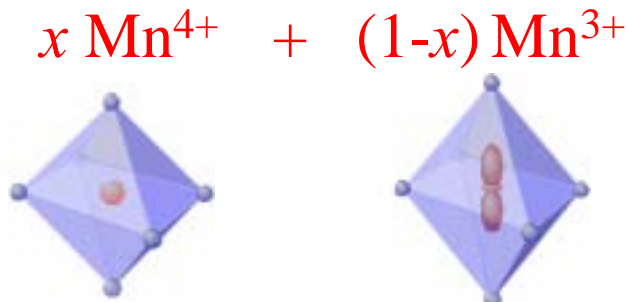
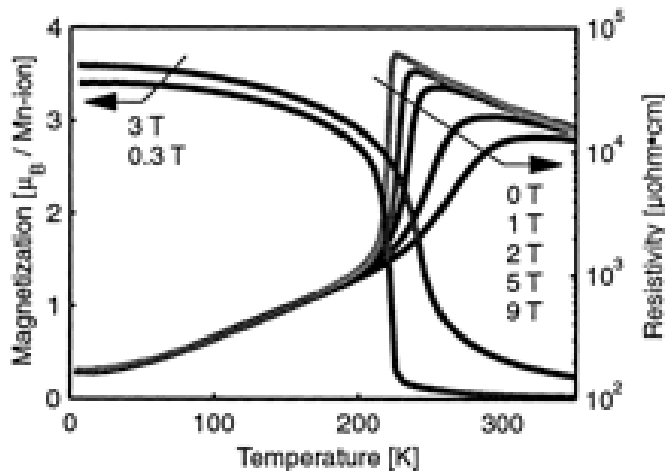
B. Campbell et al/Phys. Rev. B. **65**, 014427 (2002)

Colossal Magnetoresistance

The largest CMR effects are observed in mixed-valence manganites.

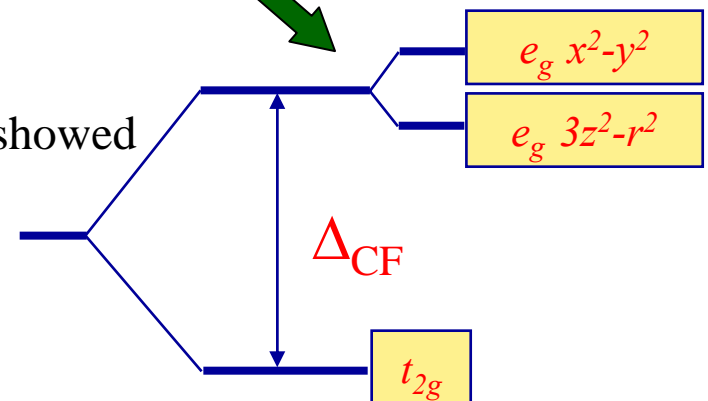
e.g. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

The CMR is largest just above the ferromagnetic transition temperature

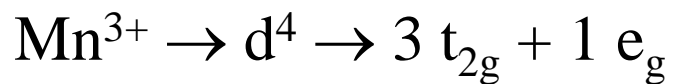
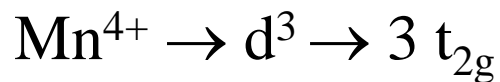
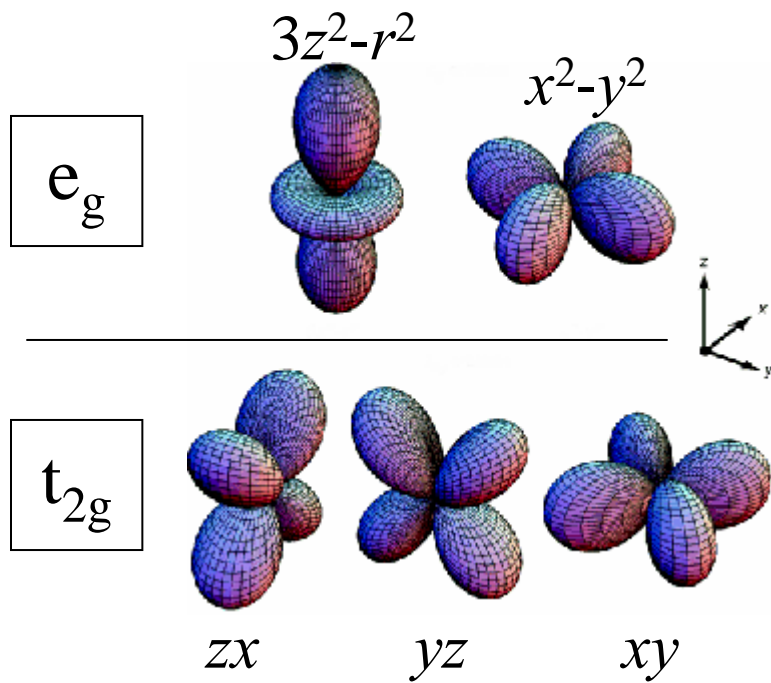


Millis, Littlewood and Shraiman [PRL 74, 5144 (1995)] showed that double exchange was not enough to explain CMR
i.e. electrons are localized by local lattice distortions

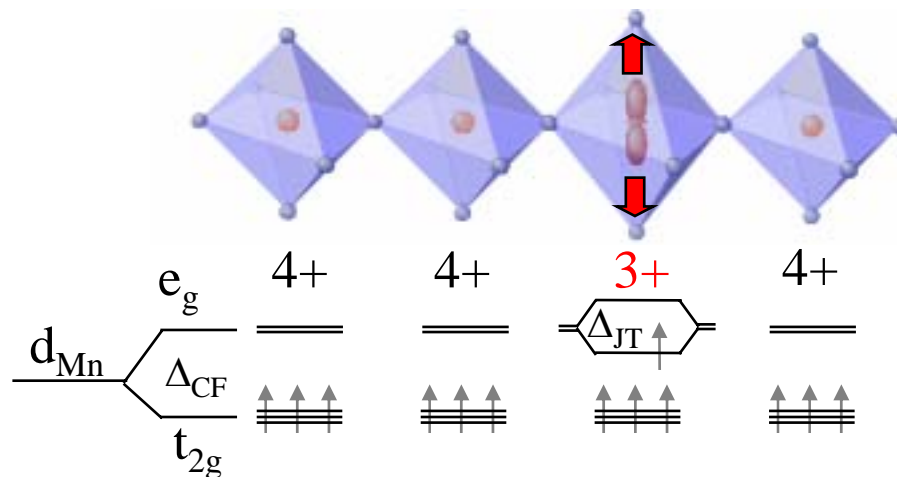
Jahn-Teller Polarons



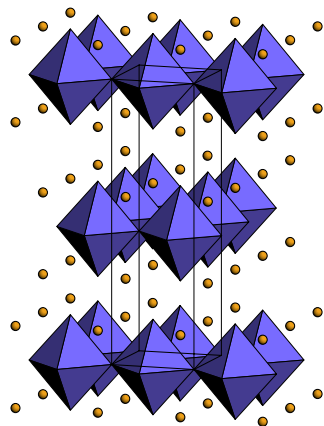
Jahn-Teller Distortions



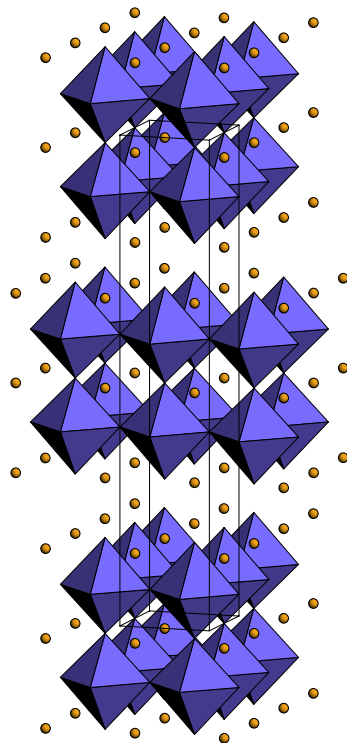
Hopping e_g electrons coupled to the lattice via the Jahn-Teller distortion mechanism.



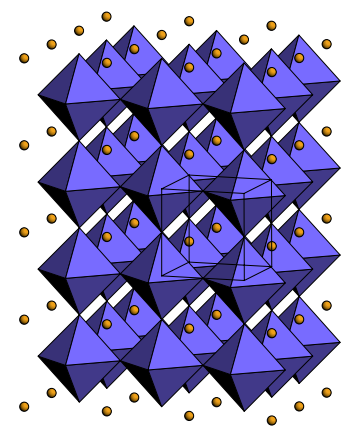
Ruddlesden-Popper Phases



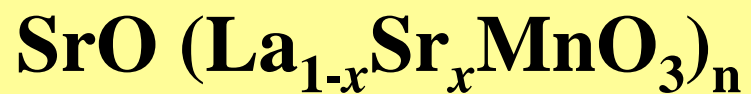
$$n=1$$



$$n=2$$



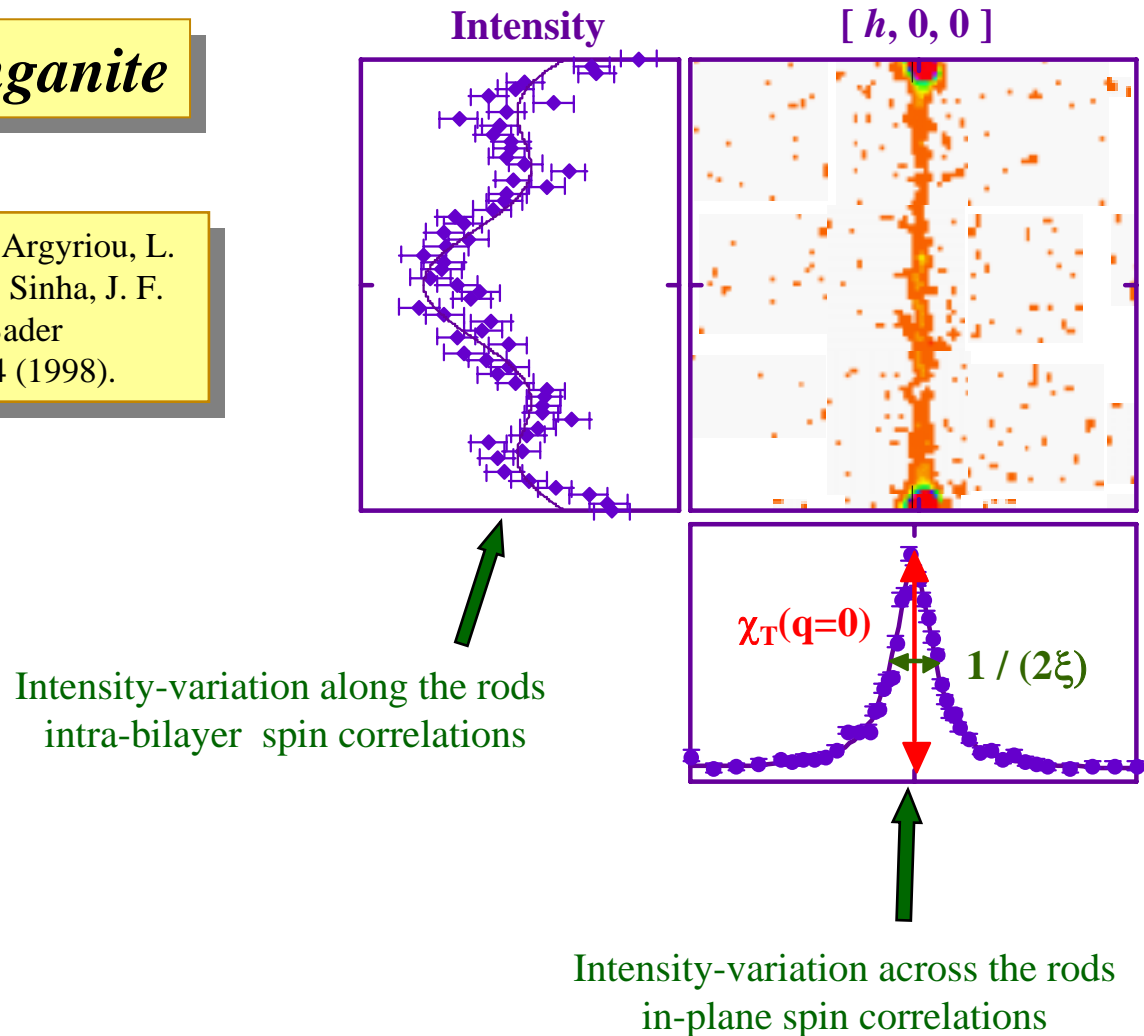
$$n=\infty$$



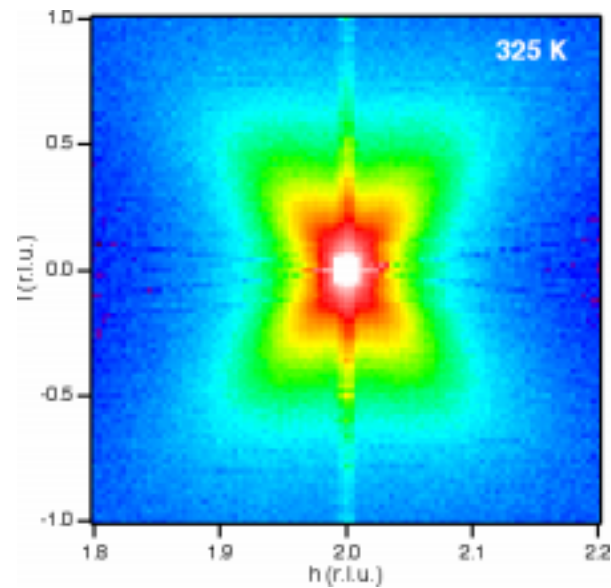
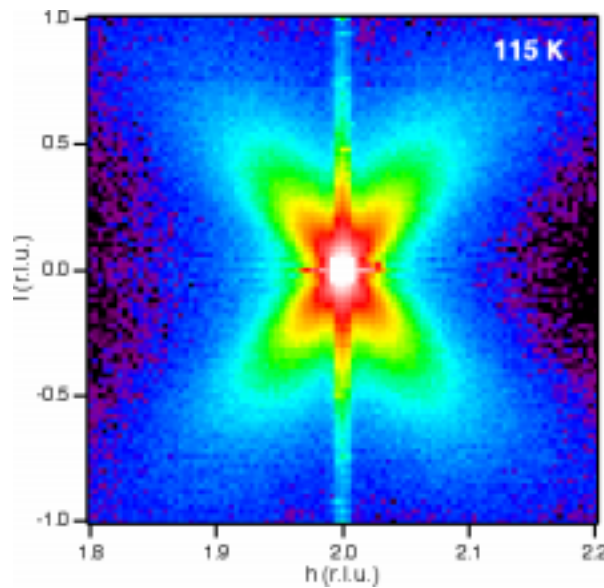
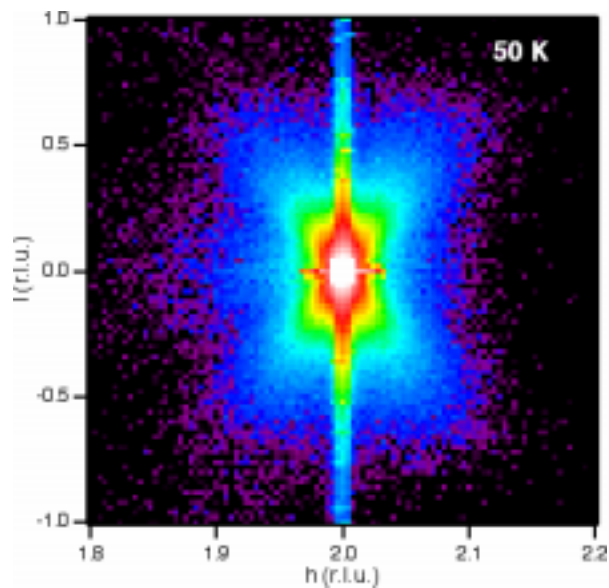
Two-dimensional Magnetic Correlations

$x=0.4$ Bilayer Manganite

R. Osborn, S. Rosenkranz, D. N. Argyriou, L. Vasiliu-Doloc, J. W. Lynn, S. K. Sinha, J. F. Mitchell, K. E. Gray, and S. D. Bader
Physical Review Letters **81**, 3964 (1998).



Huang Scattering



11-ID-D, 30keV

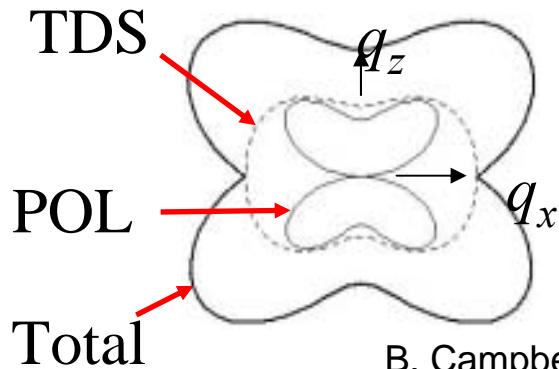
Huang Scattering Theory

$$I(\mathbf{Q}) = \sum_{m,n} e^{i\mathbf{Q} \cdot (\mathbf{R}_m - \mathbf{R}_n)} f_m f_n e^{-W_m} e^{-W_n} \langle (\mathbf{Q} \cdot \mathbf{u}_m)(\mathbf{Q} \cdot \mathbf{u}_n) \rangle$$

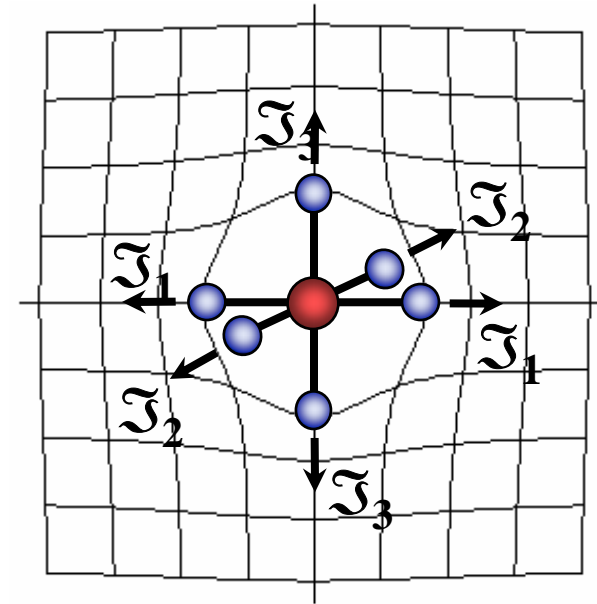
$$I_{POL}(\mathbf{Q}) = N |F_G|^2 \sum_{\alpha,\beta,\gamma,\delta} \mathcal{Q}_\beta \mathcal{Q}_\delta \left(\sum_{j,j'} \frac{\epsilon_{\alpha,\mathbf{q},j} \epsilon_{\beta,\mathbf{q},j}^* \epsilon_{\gamma,\mathbf{q},j'}^* \epsilon_{\delta,\mathbf{q},j'}}{\omega_{\mathbf{q},j}^2 \omega_{\mathbf{q},j'}^2} \right) \sum_{m,n} \mathfrak{T}_{m,\alpha} \mathfrak{T}_{n,\gamma} e^{i\mathbf{q} \cdot (\mathbf{R}_m - \mathbf{R}_n)}$$

$$I_{TDS}(\mathbf{Q}) = N |F_G|^2 \left(\frac{kT}{2M} \right) \sum_{\beta,\delta} \mathcal{Q}_\beta \mathcal{Q}_\delta \left(\sum_j \frac{\epsilon_{\beta,\mathbf{q},j}^* \epsilon_{\delta,\mathbf{q},j}}{\omega_{\mathbf{q},j}^2} \right)$$

$$u_{m,\delta} = \int \frac{d^3 q}{\left(\frac{2\pi}{a}\right)^3} \sum_{\beta} \left(\sum_j \frac{\epsilon_{\beta,\mathbf{q},j}^* \epsilon_{\delta,\mathbf{q},j}}{\omega_{\mathbf{q},j}^2} \right) \sum_n \mathfrak{T}_{n,\beta} e^{i\mathbf{q} \cdot (\mathbf{R}_m - \mathbf{R}_n)}$$



B. Campbell et al/Phys. Rev. B. **67**, 020409 (2003)



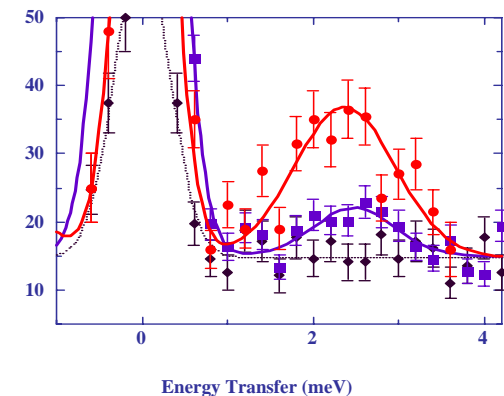
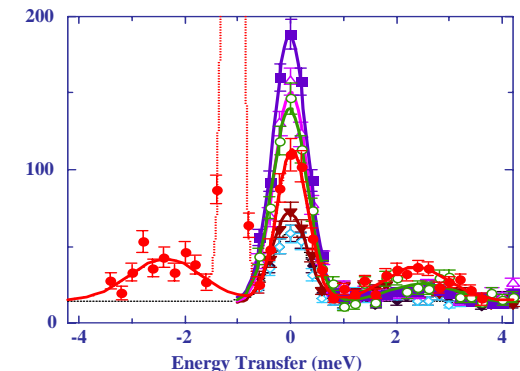
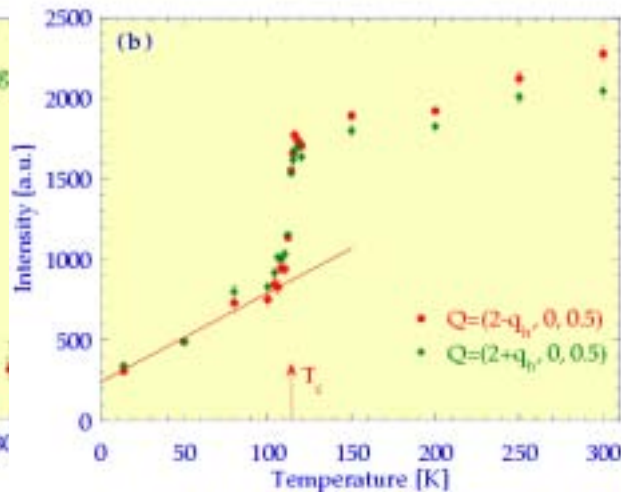
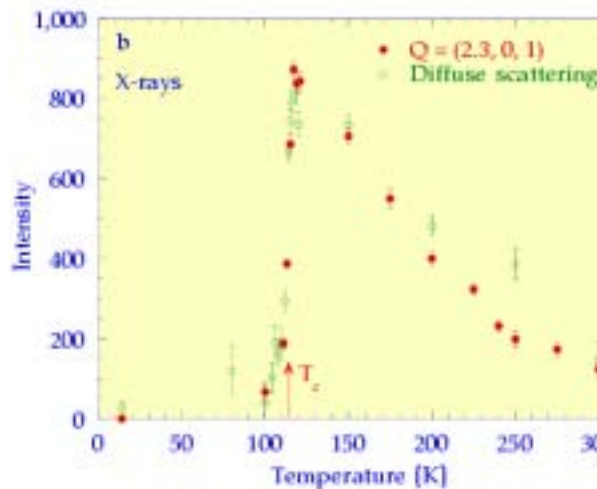
Static vs Thermal Diffuse Scattering

Inelastic Neutron Scattering

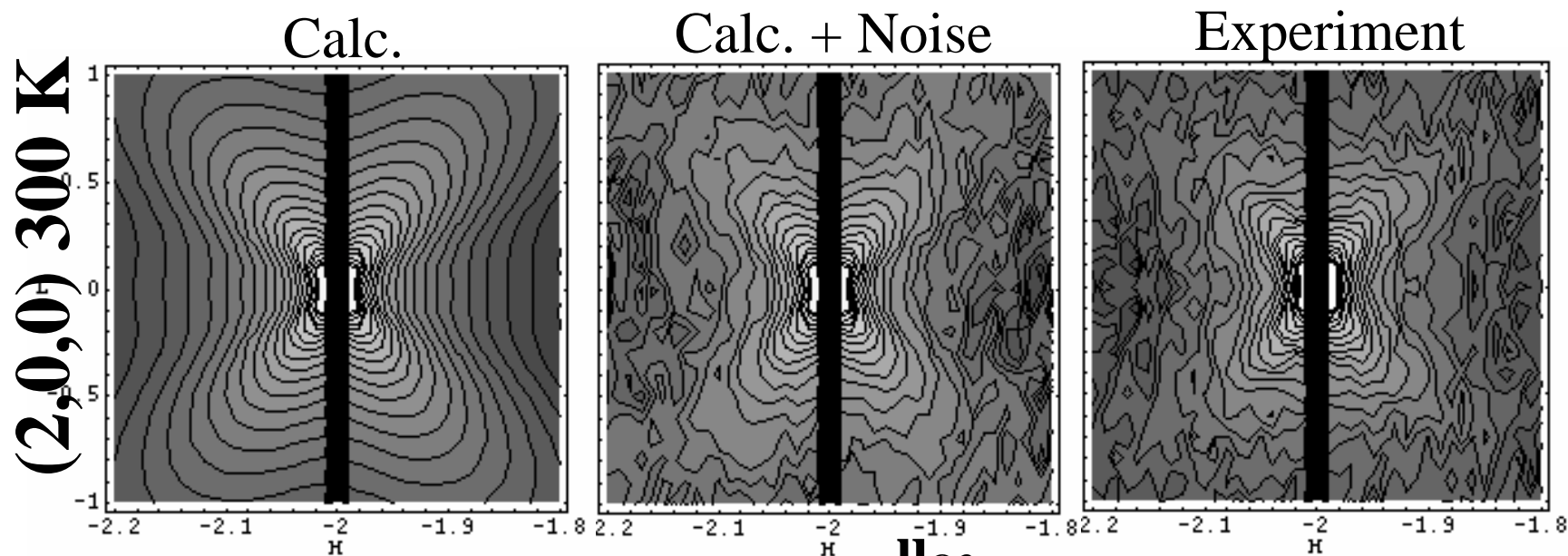
- Sudden increase in static diffuse scattering at T_C ,
- Conventional thermal population of phonons.

X-ray Scattering

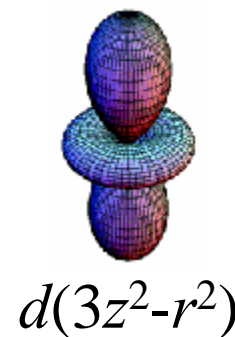
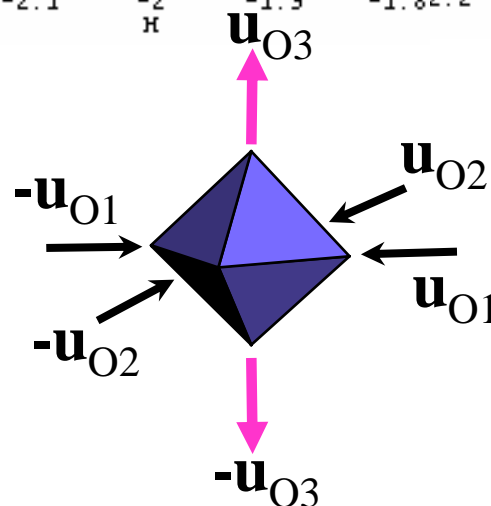
- Linear increase below T_C (thermal diffuse scattering)
- Sudden increase at T_C (static diffuse scattering)



Orbital Polarization - 300K



$$\begin{pmatrix} u_{O1_x} \\ u_{O2_y} \\ u_{O3_z} \end{pmatrix} = \begin{pmatrix} -0.012 \\ -0.012 \\ 0.074 \end{pmatrix} \text{Å}$$



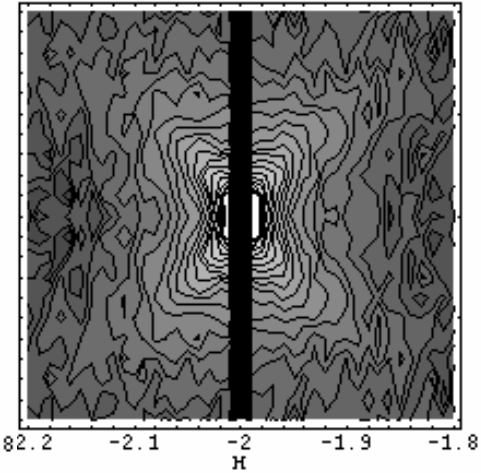
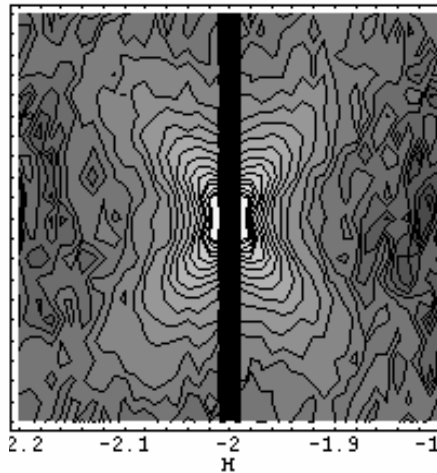
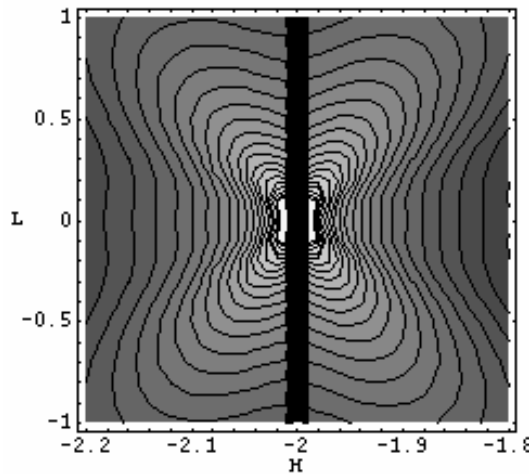
Temperature Dependence of Polarization

(2,0,0) 300 K

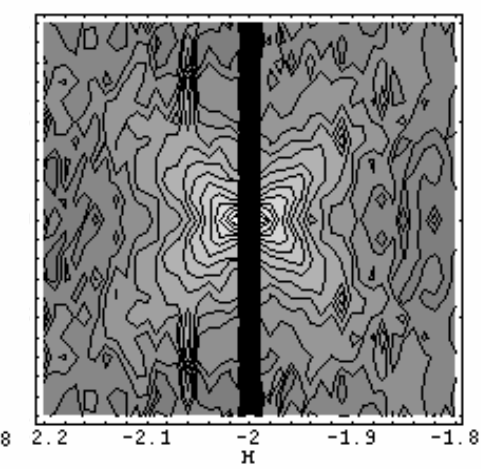
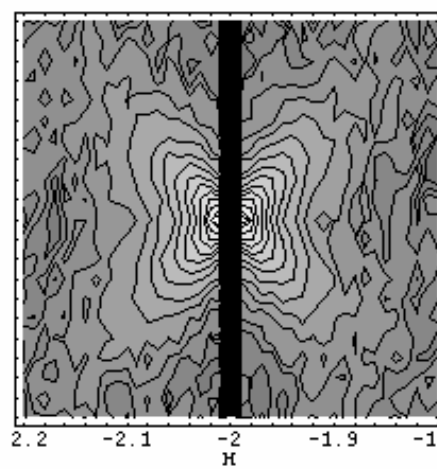
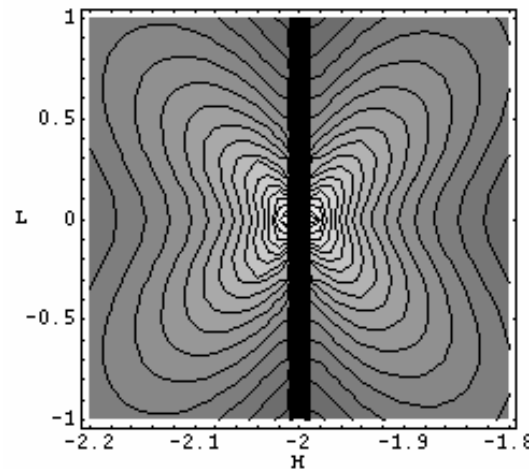
Calc.

Calc. + Noise

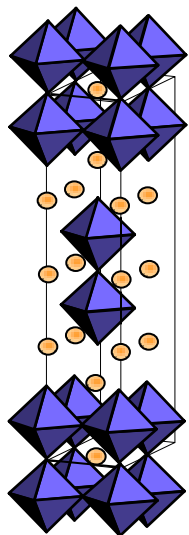
Experiment



(2,0,0) 120 K

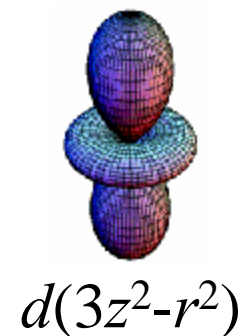
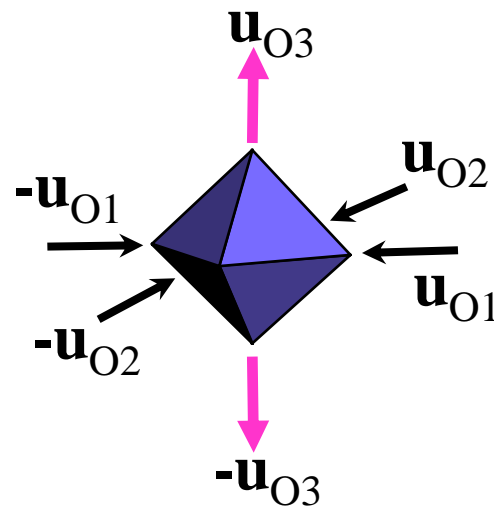


Orbital Polarization



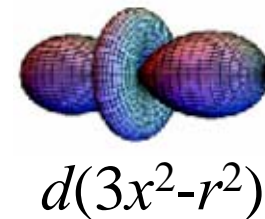
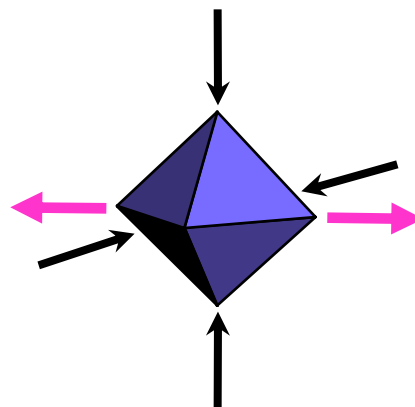
300 K

$$\begin{pmatrix} u_{O1_x} \\ u_{O2_y} \\ u_{O3_z} \end{pmatrix} = \begin{pmatrix} -0.012 \\ -0.012 \\ 0.074 \end{pmatrix} \text{Å}$$



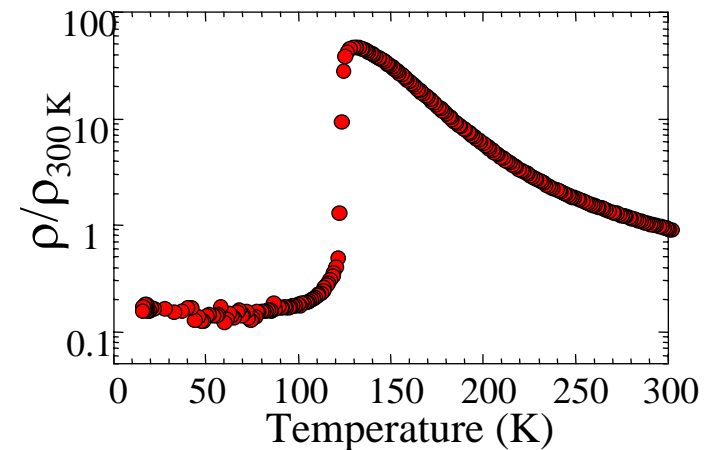
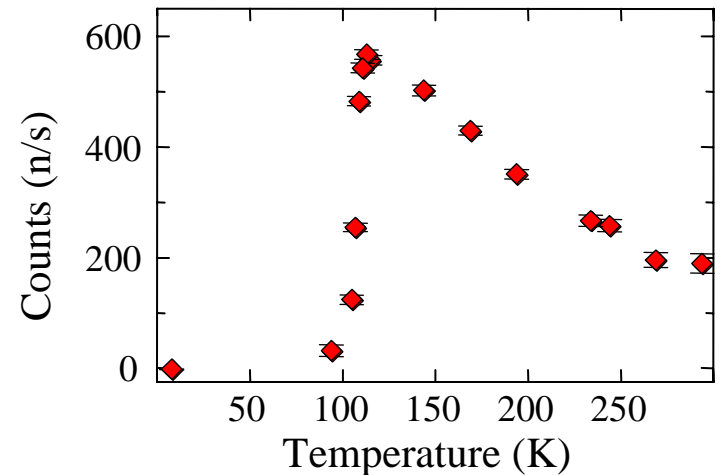
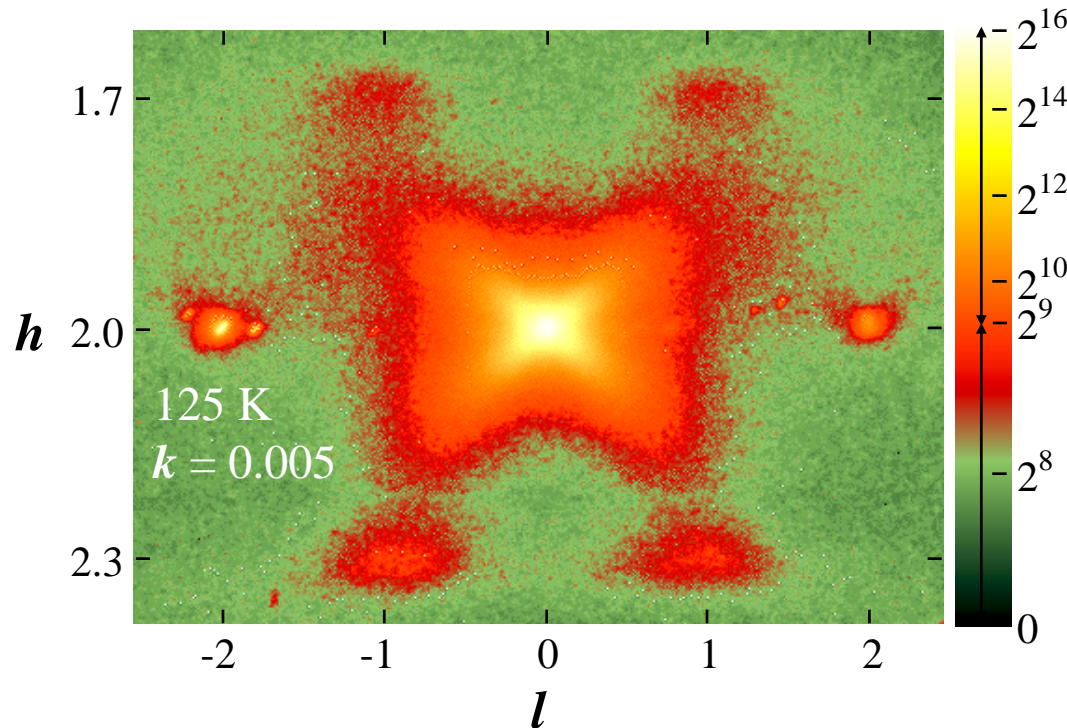
120 K

$$\begin{pmatrix} u_{O1_x} \\ u_{O2_y} \\ u_{O3_z} \end{pmatrix} = \begin{pmatrix} 0.083 \\ -0.022 \\ -0.023 \end{pmatrix} \text{Å}$$



Evidence of Polaron Correlations

Bruker CCD x-ray data: 115 keV 11-ID-C



L. Vasiliu-Doloc *et al* (PRL 1999)

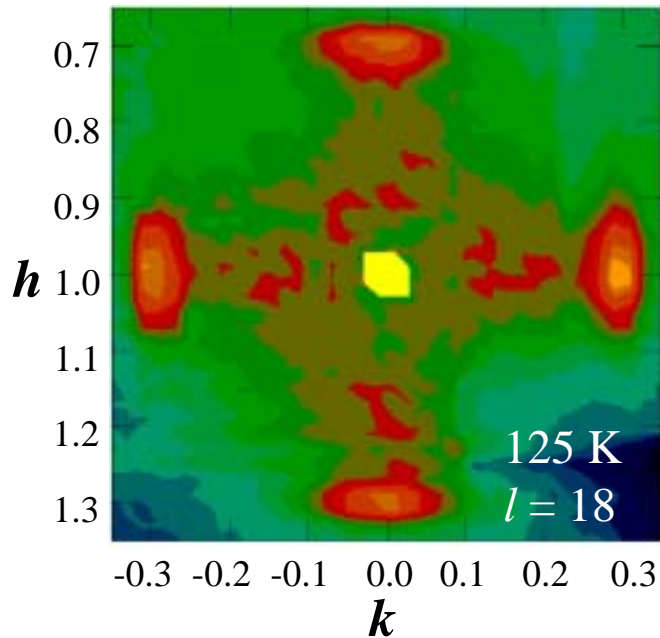
Shimomura *et al* (PRL 1999)

Adams *et al* (PRL 2000), Dai *et al* (PRL 2000)

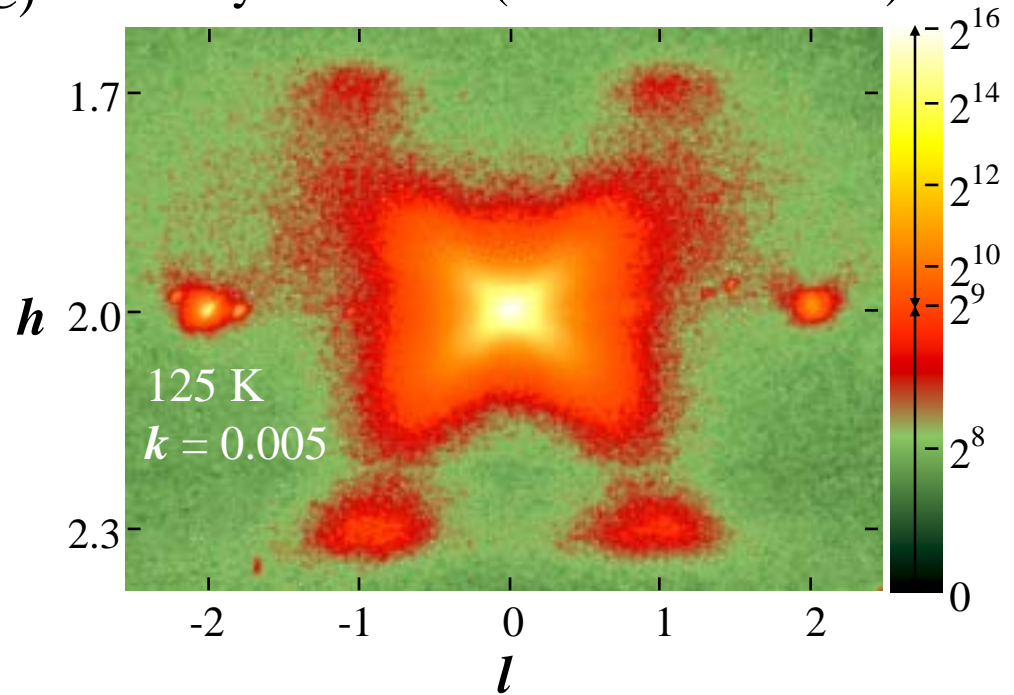
Kiriyukin *et al* (PRB 2002)

Models of Polaron Correlations

x-ray SCD data (36 keV 1-ID-C)



X-ray SCD data (115 keV 11-ID-C)



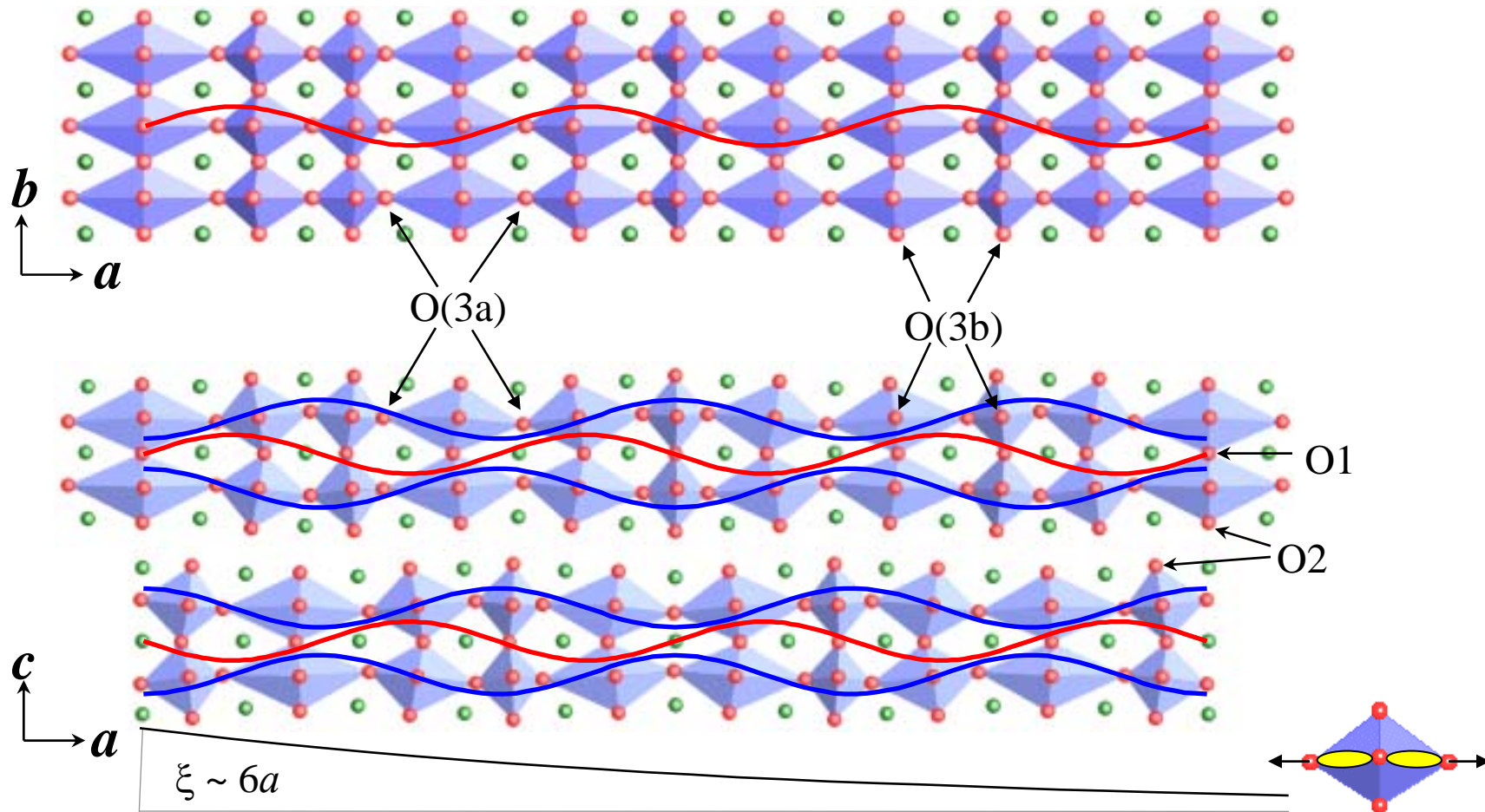
- 1D modulation along (1 0 0)
- $\mathbf{q} = (0.3 \ 0 \ \pm 1)$ or $(0.3 \ 0 \ 0)$
- 109 unique 1st-order satellites

$$I(hklm) \propto |F|^2 = \left| \pi(\mathbf{G} + m\mathbf{q}) \cdot \sum_n \mathbf{u}_n f_n e^{i\mathbf{G} \cdot \mathbf{r}_n} \right|^2$$

$$\mathbf{G} = (hkl) \quad \mathbf{u}_n = \mathbf{u}_n^c + i\mathbf{u}_n^s$$

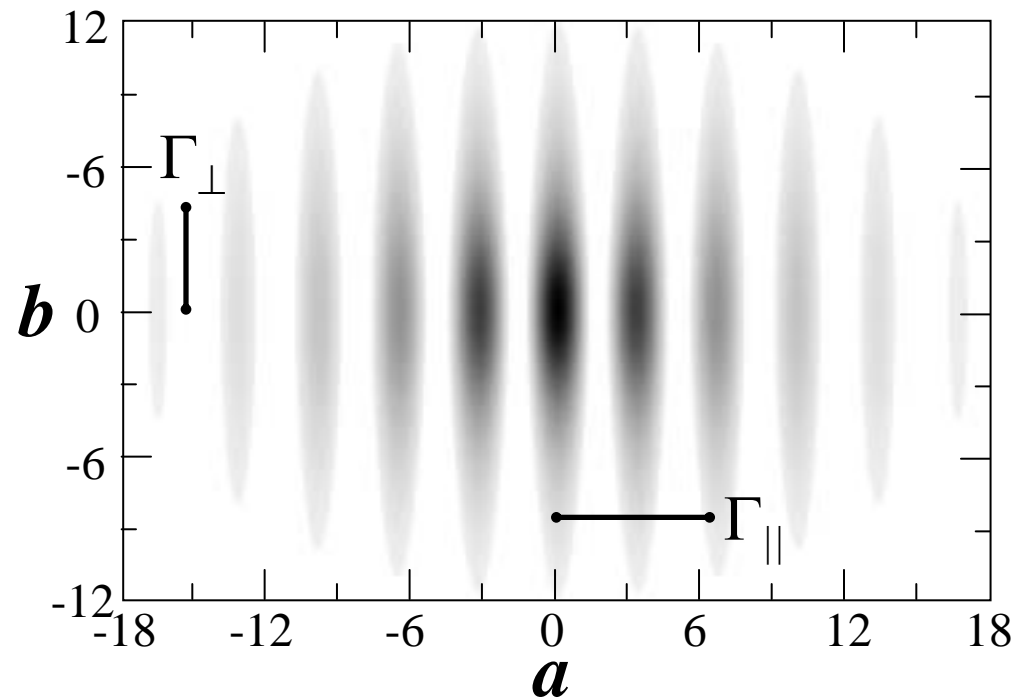
$$\Delta \mathbf{r}_n = \mathbf{u}_n^s \sin(\mathbf{q} \cdot \mathbf{r}_n) + \mathbf{u}_n^c \cos(\mathbf{q} \cdot \mathbf{r}_n)$$

Longitudinal Jahn-Teller Modulations



B. J. Campbell, R. Osborn, D. N. Argyriou, L. Vasiliu-Doloc, J. F. Mitchell, S. K. Sinha, U. Ruett, C. D. Ling, Z. Islam, and J. W. Lynn, *Physical Review B* **65**, 014427 (2001).

Correlated Polaronic Fluid



Unanswered Questions

- What is the origin of the orbital stripes and why are they not seen in the perovskites?
- How does ferromagnetism coexist with polaron correlations and why is the exchange enhancement so small?

$$\mathbf{q} \approx (0.3, 0, 0)$$

$$\xi_x \approx 6 a \approx 23 \text{ \AA}$$

$$\xi_y \approx 4 a \approx 15 \text{ \AA}$$

$$\xi_z \approx c/2 \approx 10 \text{ \AA}$$

Speculations

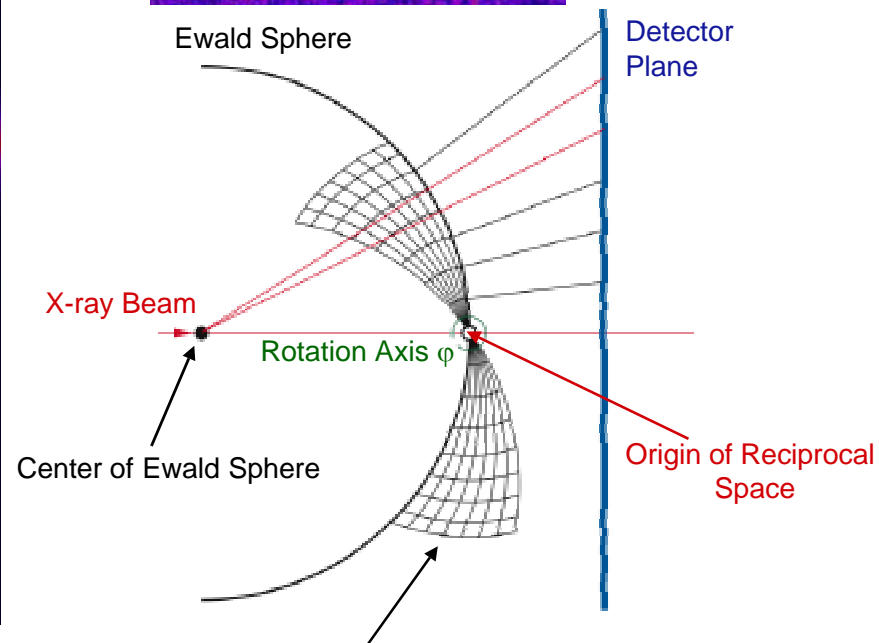
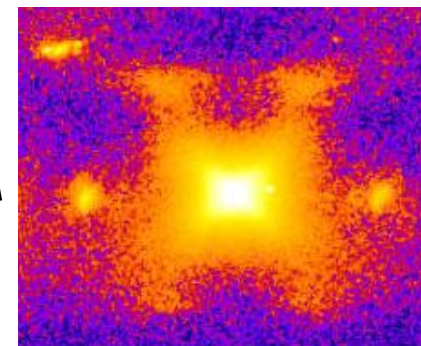
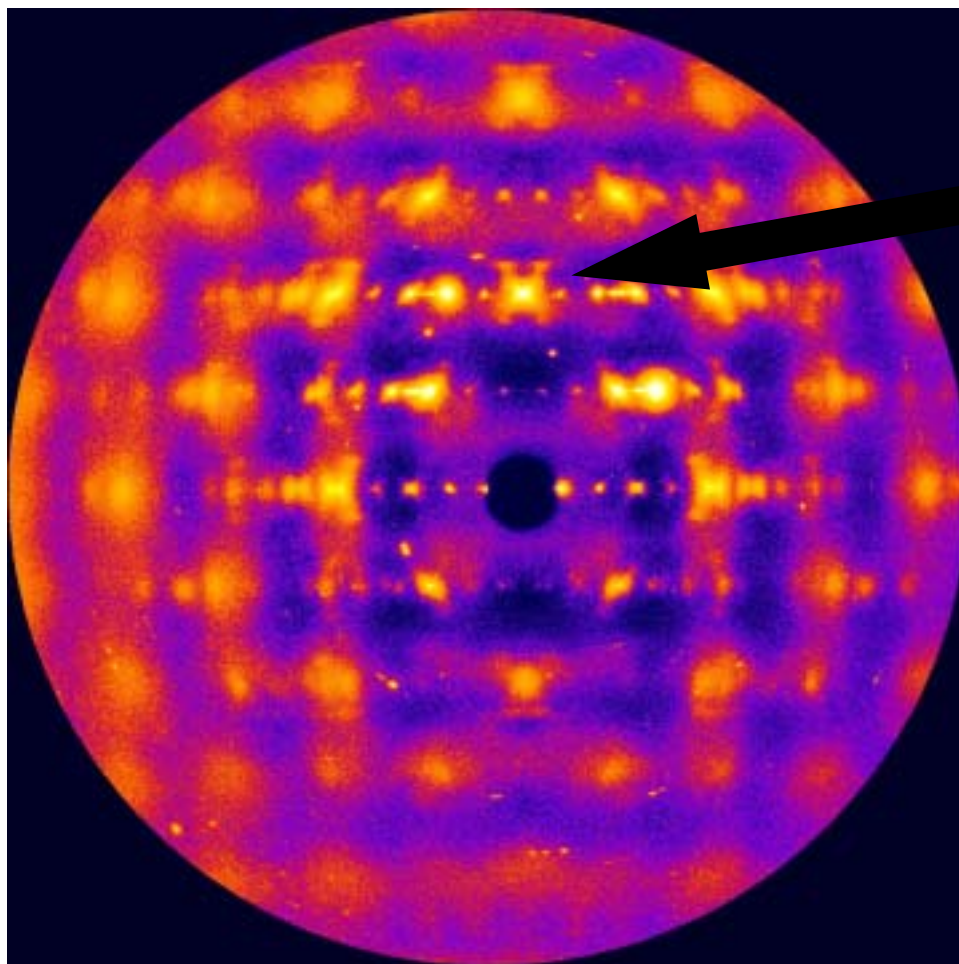
- Stripe formation could be driven by
 1. Competition of Coulomb and strain interactions
 2. CDW-like instability of a pseudogapped metal

N.B. Importance of reduced dimensionality

Potential of High-Energy Diffuse X-rays

- **Reasons for using high-energy X-ray diffuse scattering**
 - Need for very wide dynamic range of intensities and Q:
 - *Diffuse scattering is several orders of magnitude weaker than Bragg scattering. significantly weaker compared to Bragg reflections.*
 - *It is spread over very large volumes of reciprocal space so we must minimize corrections for absorption, background, & Compton scattering.*
- **Technical Demands**
 - Detector technology
 - *background vs detector saturation vs read-out times*
 - *Single Detector (4h) → Image Plate (2m) → CCD (4s) → GE (0.03s)*
 - Data analysis on large volumes of data
 - Thermal Diffuse Scattering co-existing with static diffuse scattering.
- **Ultimate Goal**
 - to collect complete *quantitative* volumes of reciprocal space efficiently.
 - *to allow modelling of complex disorder*
 - *to allow parametric studies of defects and their correlations.*

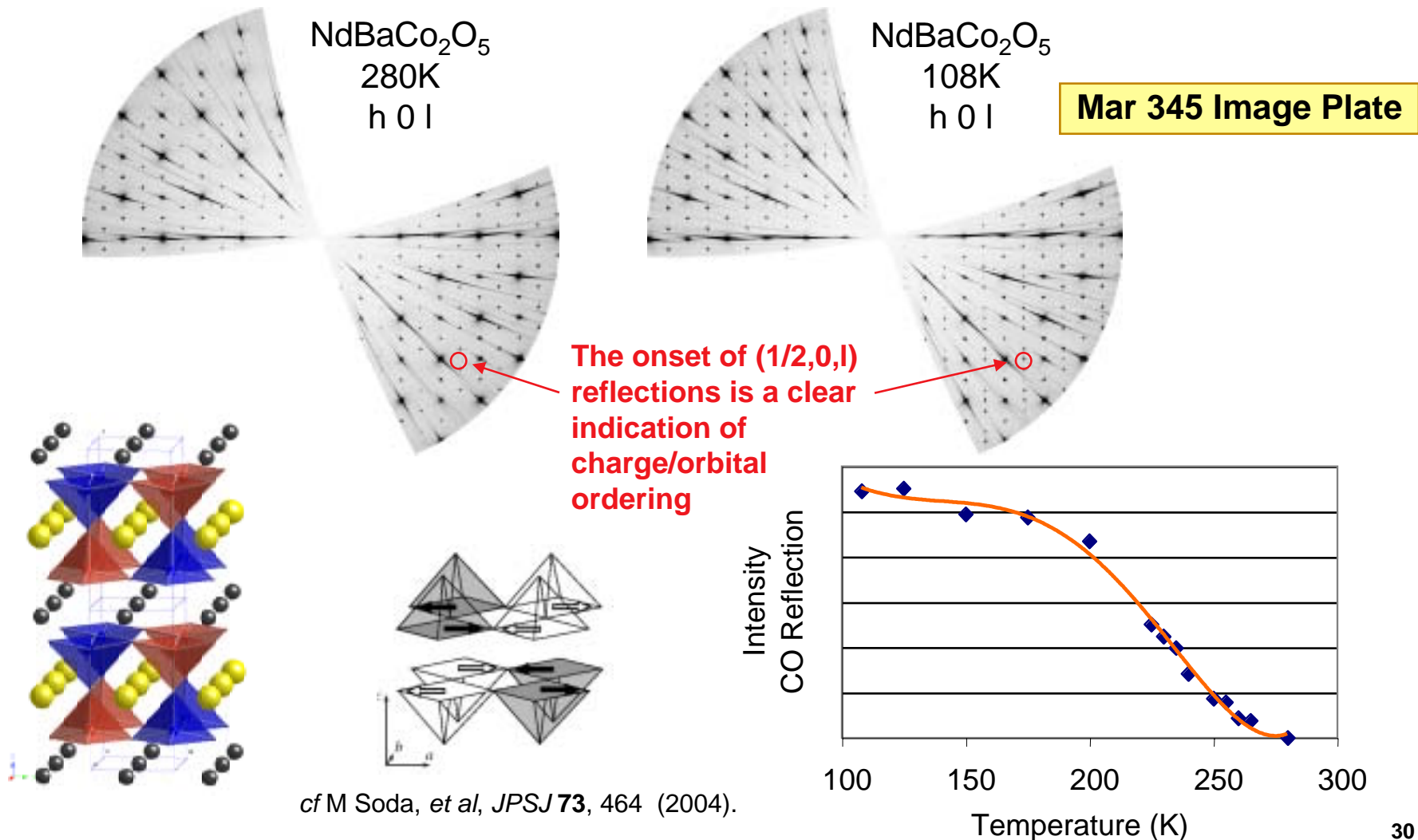
Efficiency of Area Detectors



Mar 165 CCD ~ 1-ID-C

M. A. Estermann, W. Steurer, *Phase Transitions* **67**, 165 (1998)
M. A. Estermann, *et al*, *Z. Krist.* **215**, 584 (2000)

Superlattice Reflections in a Layered Cobaltite

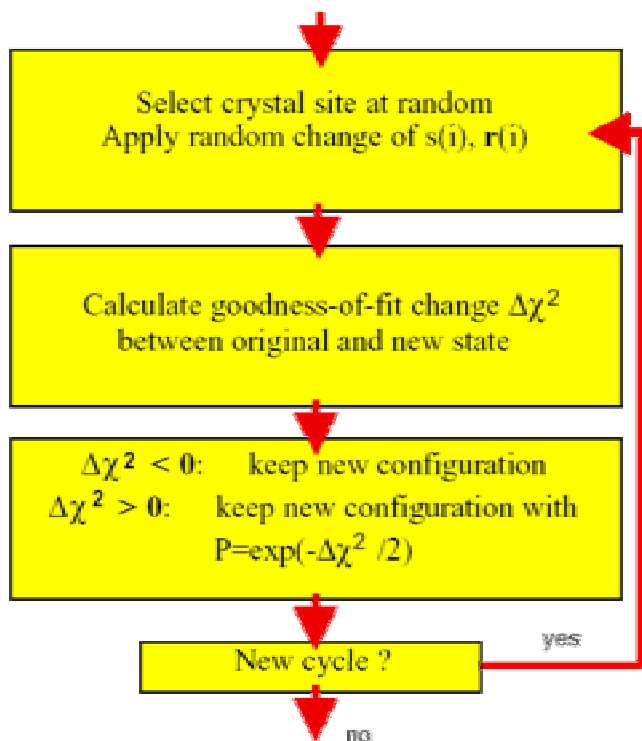


Diffuse Scattering Data Analysis

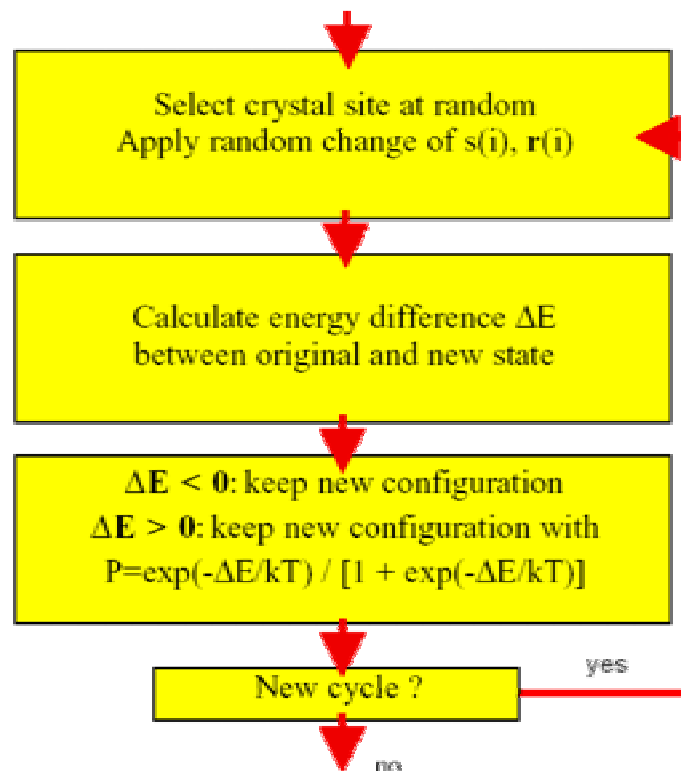
- **Diffuse scattering from single crystals requires sophisticated analysis strategies to cope with large data sets**
 - A full rotation volume with equivalent in-plane resolution ~ 7.2GB
- **This is equivalent to**
 - Rietveld analysis 30 years ago
 - Inelastic scattering now
- **Future developments in instrumentation and data analysis will make data treatment much easier, providing for an expansion of the user community.**
- **X-ray diffuse scattering is complementary to neutron diffuse scattering in many systems. Analysis tools should be developed in coordination with neutron sources.**

Reverse vs Automatic Monte Carlo

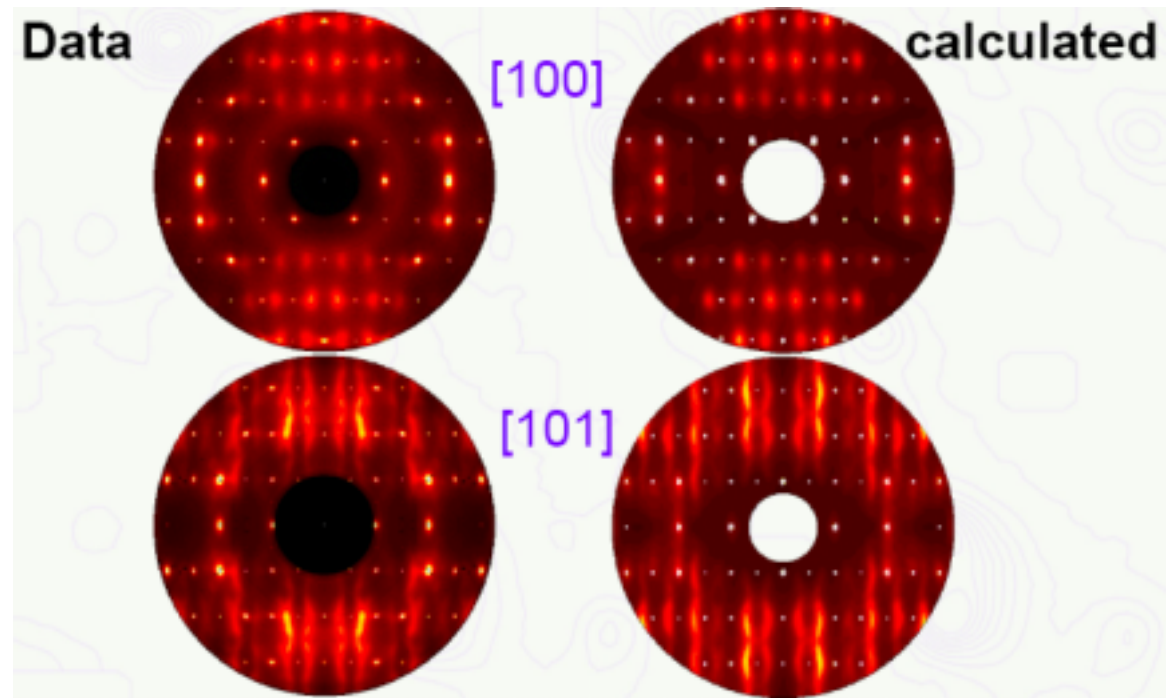
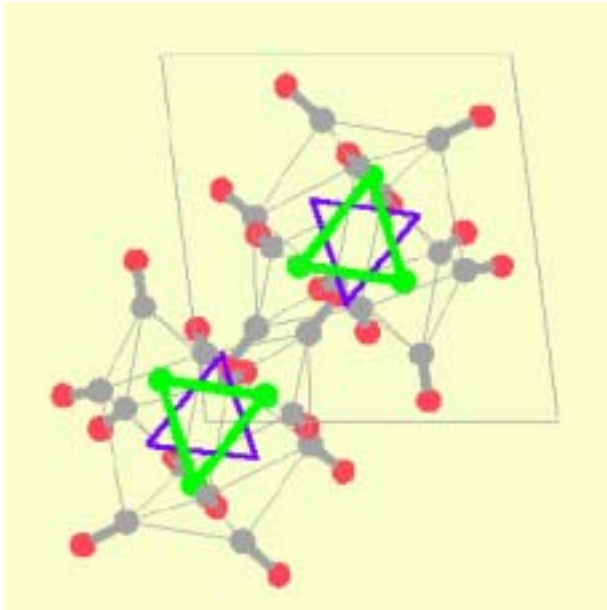
Reverse Monte Carlo



Automatic Monte Carlo



Disorder in $\text{Fe}_3(\text{CO})_{12}$ - Automatic Monte Carlo



Welberry, Proffen and Bown, Acta Cryst A54, 661 (1998)

Thermal Diffuse Scattering

VOLUME 83, NUMBER 16

PHYSICAL REVIEW LETTERS

18 OCTOBER 1999

Determination of Phonon Dispersions from X-Ray Transmission Scattering: The Example of Silicon

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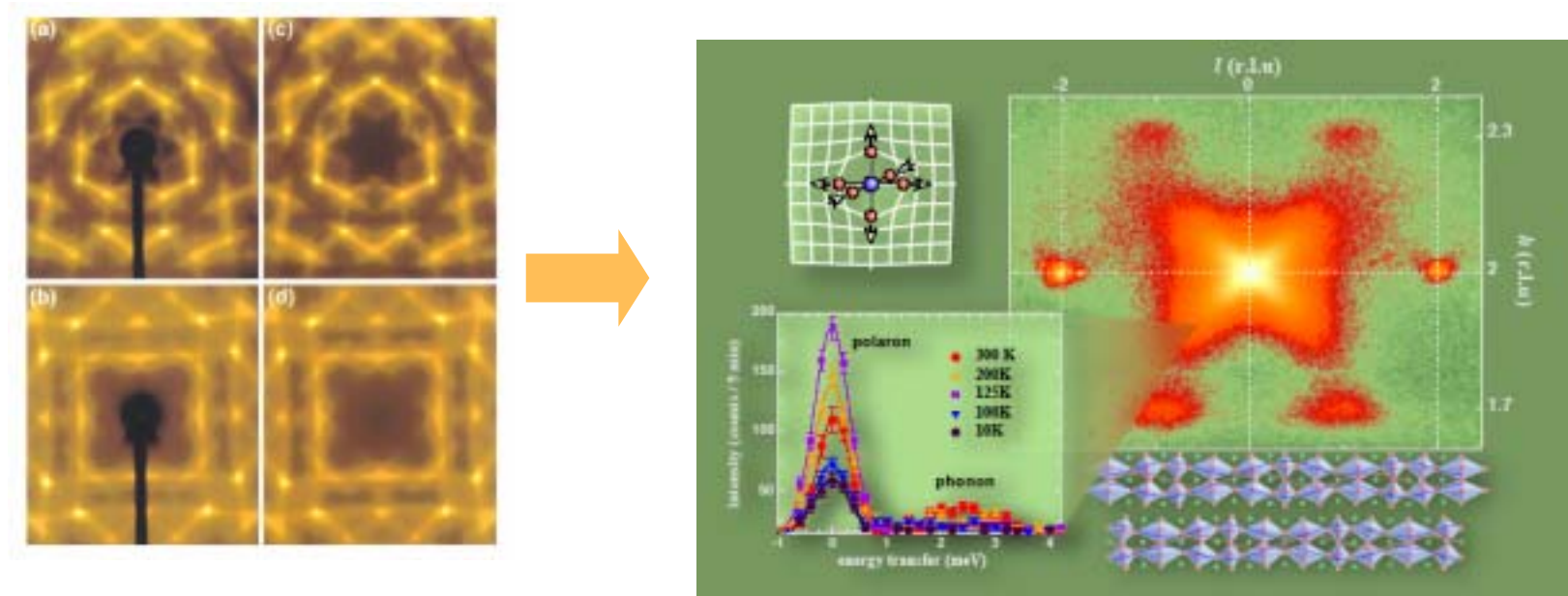
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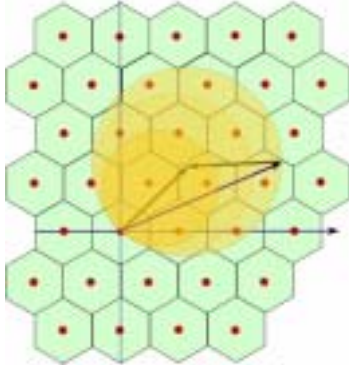
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(Received 6 May 1999)



Diffuse Neutron Scattering Proposal at SNS

TOF Laue Diffractometer



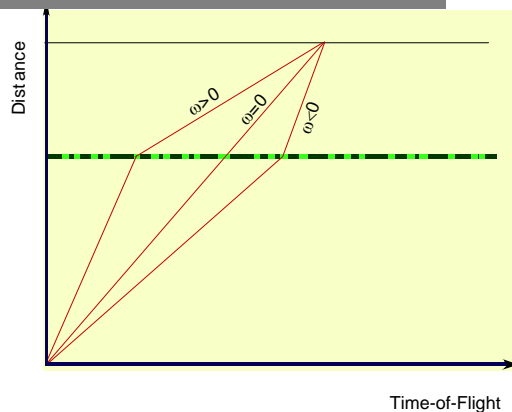
i



“combine white beam and fixed k_i ”

1. TOF Laue Diffractometer
 - highly efficient data collection
 - wide dynamic range in Q
2. Statistical Chopper
 - elastic energy discrimination
 - optimum use of white beam

Statistical Chopper



$$C(j,k) = \sum_{i=i_{\min}}^{i_{\min}+N} A(i-k)S(i,j-i) + B(j)$$

$$S(i,j) = \frac{2}{N+1} \sum_{k=1}^N A(i-k)C(i+j,k) - \frac{2}{N+1} B(i+j)$$

Conclusions

- **Single crystal diffuse scattering provides vital information on complex disorder, and can make important contributions to a large number of scientific fields.**
- **Advances in instrumentation and analysis tools will open the technique up to a much larger range of scientific community.**
 - Detector technology must cope with a very wide dynamic range
 - Computational analysis must cope with huge volumes of data
- **High-Energy X-rays are a vital part of this development because**
 - large volumes of reciprocal space can be measured efficiently.
 - absorption and background corrections are minimized.
- **This should be pursued in parallel with complementary developments in neutron instrumentation.**